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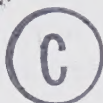
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INFRA-RED SPECTRA OF ETHYLENE OXIDE CLATHRATE HYDRATE

BY



DAVID ALAN OTHEN

A THESIS

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The undersigned certify that they have read, and
recommend to the Faculty of Graduate Studies and Research,
for acceptance, a thesis entitled

'INFRA-RED SPECTRA OF ETHYLENE OXIDE CLATHRATE HYDRATE'

submitted by DAVID ALAN OTHEN in partial fulfilment of the
requirements for the degree of Doctor of Philosophy.

ABSTRACT.

Spectra of well characterized, powdered ethylene oxide clathrate hydrate at 100°K have been recorded from 4000 to 17cm^{-1} . Samples were prepared by several techniques from solutions of ethylene oxide (E.O.) in H_2O or D_2O containing from 0 to 10% HDO. The effects of small amounts of ice or solid E.O. on the spectra are discussed.

The absorptions by the intramolecular, rotational and translational vibrations of the water molecules are assigned by comparison with the spectra of the ices. The spectral similarities between ice I and the hydrate show that the host is orientationally disordered and indicate that the structural differences do not markedly affect either the density of states curves or the intensity distribution functions for any of these vibrations. The absorption by the translational vibrations of the water molecules has no features attributable to factor group allowed transitions. Therefore, the μ_{ave} term, used in the theory for translational vibrations in orientationally disordered crystals, is small for the hydrate. The frequencies of maximum far infra-red absorption in E.O. hydrate and the ices are related to the weighted mean O-O hydrogen bond distances, while the breadth indicates the range of these distances. The $\nu_{\text{OD}}(\text{HDO})$ bandshape is very sensitive to HDO ice in the sample. A plot of frequency of $\nu_{\text{OD}}(\text{HDO})$ against weighted mean O-O bond distance for the different phases gives two straight lines, one for ordered

and one for disordered phases, but the halfwidths are less^{ii.} easily interpreted.

The absorptions by intramolecular E.O. vibrations are compared with the mid-infra-red spectra of gaseous, liquid and solid E.O. and the Raman spectrum of liquid E.O. The frequencies of the A_1 CH_2 stretching and wagging modes and of the B_1 ring vibration in E.O. gas are reassigned, and the intramolecular E.O. absorptions in the clathrate are assigned. The E.O. frequencies in the clathrate are close to those of liquid E.O. but the bands are sharper. Therefore, either the E.O. motion in the two phases differs sufficiently to cause the change in halfwidth, or the halfwidth is not significantly influenced by molecular reorientation in the absence of intermolecular coupling. The A_1 ring breathing mode is a doublet with two satellite bands and the overlapping A_1 and B_1 ring deformations couple with the rotational oscillations of the water molecules. No other splitting or coupling is detected. The reasons for this are not clearly understood, but these results may indicate that weak interaction occurs between the E.O. oxygen atom and the host molecules. The absorption by intermolecular E.O. vibrations is tentatively assigned as a broad band from 100cm^{-1} to low frequency, centred at 50cm^{-1} . No features are definitely attributable to absorption by E.O. in the pentagonal dodecahedral cages.

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CHAPTER 1. INTRODUCTION TO THE CLATHRATE HYDRATES.

1.1 Inclusion Compounds and the Clathrate Hydrates.

Inclusion compounds are solids in which one component entraps a second substance. They have been the object of scientific research for nearly two centuries (1). Indeed the familiar laboratory test for iodine, which uses starch, relies on the creation of an intense blue colour when the iodine molecules align themselves in channels in the starch (2). Zeolites, molecular sieves and many other compounds are of great importance in the separation and purification of chemical compounds (3).

In 1947 Palin and Powell (4) studied the molecular compound of sulphur dioxide and hydroquinone (β -quinol). They deduced from the X-ray diffraction pattern that its structure consists of two three-dimensional interpenetrating lattices of hydrogen-bonded β -quinol molecules. These two lattices are intermeshed to form isolated cages inside which sulphur dioxide molecules are imprisoned, one per cage. A year later Powell (5) used the term clathrate to describe this type of inclusion compound.

Clathrates are therefore inclusion compounds in which one component forms a three-dimensional lattice containing cage-like cavities, inside which individual molecules of other substances are isolated. The lattice component is called the host and the encaged substance

is the guest.

Table I illustrates some of the guest-host systems in clathrates. The references cited form only a small part of the literature on clathrates. In the last example, the host molecule is water and the compounds are known as clathrate hydrates.

1.2 The Discovery of Clathrate Hydrates and the Study of their Stoichiometry.

Sir Humphry Davy in the Bakerian Lecture to the Royal Society of London in 1810 (43) said that;

" It is generally stated in chemical books, that oxymuriatic gas (chlorine) is capable of being condensed and crystallized at a low temperature; I have found by several experiments that this is not the case. The solution of oxymuriatic gas in water freezes more readily than pure water, but the pure gas dried by muriate of lime (calcium chloride) undergoes no change whatever, at a temperature of 40 below 0° of FAHRENHEIT. The mistake seems to have arisen from the exposure of the gas to cold in bottles containing moisture."

Thus although crystals of chlorine hydrate had inadvertently been formed by earlier research workers, Davy was the first to realize that this solid was only formed in the presence of water.

Thirteen years later, Faraday (44) took advantage of the prolonged cold winter to procure crystals of chlorine hydrate for analysis. He described the preparation of the bright yellow crystals (45) and noted that chlorine hydrate can be made to sublime within the

TABLE I. GUEST-HOST SYSTEMS IN CLATHRATES.

<u>HOST</u>	<u>GUESTS INCLUDE</u>	<u>REFERENCES</u>
β -quinol (hydroquinone).	HCl, SO ₂ , H ₂ S, CO ₂ , CO, Ar, Kr, Xe, N ₂ , NO, O ₂ , H ₂ , CH ₄ , CHF ₃ , NF ₃ .	6 - 11
Phenol.	H ₂ S, HCl, HBr, CO ₂ , CH ₃ Br, CH ₂ Cl ₂ .	12 - 13
Dianin's Compound.	C ₆ H ₅ Br, C ₆ F ₅ CH ₃ ,	
4-p-hydroxy -	C ₂ H ₅ OH, HCOOH, NH ₃ ,	
phenyl-2,2,4-	CH ₃ OH, CH ₃ I, CH ₃ COOH,	
trimethylchroman	CH ₃ (CH ₂) ₄ COOH, CH ₃ CN,	8,
and -thiachroman.	CHCl ₃ , Bromodurene.	14 - 17
Hofmann Complexes.	C ₆ H ₆ , C ₄ H ₄ S, C ₆ H ₅ NH ₂ ,	
Ni II	C ₅ H ₅ N, C ₄ H ₅ N, C ₄ H ₄ O.	
Ni II Cu II		
Ni II Zn II		
Ni II Cd II		
Cu II Pd II		
Cu II Pt II		18 - 29
Werner Complexes.	Xylenes, cumenes,	
Ni II	methylnaphthalenes,	
Fe II	dichlorobenzenes,	
Co II		
{benzylamines	methylstyrenes,	
{4-methylpyridine	p-terphenyls.	
{1-phenylethylamine}		
dithiocyanate.		30 - 34

TABLE I. Continued.

<u>HOST</u>	<u>GUESTS INCLUDE</u>	<u>REFERENCES</u>
Ni II - bisethylxanthate - {4,4'-bipyridyl 1,10-phenanthroline}.	C_6H_6 , $C_6H_5CH_3$, C_6H_5Cl , $CHCl_3$.	35
$NaAlSi_3O_8$, $CaAl_2Si_2O_8$, & other feldspathoids.	$CaCl_2$, $CaCO_3$, $CaSO_4$, $NaCl$, Na_2CO_3 , Na_2SO_4 .	36
Silicon, germanium.	Sodium.	37
Polyvinyl acetate.	Iodine.	38
Water.	Ar, N_2 , O_2 , Cl_2 , Br_2 , $BrCl$, H_2S , CS_2 , SF_6 , SO_2 , CO_2 , NO , ClO_2 , CH_4 , C_2H_6 , C_3H_8 , C_2H_4 , CH_3Cl , CH_3I , CH_2F_2 , CHF_3 , CCl_3Br , C_2H_5F , CH_3NH_2 , $(CH_2)_2O$, C_4H_8O , $(CH_3)_2CO$, $C_6H_{12}N_4$, $[(iso-C_5H_{11})_4N^+]_2WO_4^{2-}$, $[(n-C_4H_9)_4P^+]_2C_2O_4^{2-}$, $(n-C_4H_9)_3S^+F^-$, HPF_6 .	39 - 42

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preparation vessel. Faraday reported that chlorine hydrate was very nearly 27.7% chlorine and 72.3% water or $\text{Cl}_2 \cdot 10\text{H}_2\text{O}$.

During the latter part of the nineteenth century many more clathrate hydrates of simple molecules were prepared and studied (40 - 42, 46 - 49). This group of compounds attracted considerable attention, both because of the diverse chemical and physical nature of the guest molecules, and because of the variety of stoichiometries reported by different research workers.

Owing to the vast number of clathrate hydrates it is impractical to review, in this thesis, all of the work carried out on them. Extensive reviews are available (1, 40 - 42). In this section the work on the hydrates of chlorine and ethylene oxide will be used to illustrate many of the difficulties encountered during their study.

The early research workers thought that the hydrates were stoichiometric compounds and, hence frequently took inadequate precautions to avoid the incorporation of air or mother liquor into their samples. They also made little or no attempt to prevent the decomposition of the hydrates during their study. Not surprisingly, therefore, widely differing results were obtained.

Wurtz first prepared ethylene oxide hydrate in 1863 (46) by cooling a solution of ethylene oxide in water until a mass of transparent crystals was deposited at a

temperature just above 0°C . He suggested that these crystals were ethylene oxide hydrate, but he was unable to determine their composition. It was over fifty years before ethylene oxide hydrate was studied again (50).

Faraday's preparation of chlorine hydrate was repeated in 1878 by Isambert (51) who measured the dissociation pressure of the hydrate between 0 and 14.5°C . In 1883 Mauméné (52) prepared chlorine hydrate from water-rich and from chlorine-rich mixtures. His analysis showed that when excess water was present $\text{Cl}_2 \cdot 12\text{H}_2\text{O}$ was the product, but when excess chlorine was present then $\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ was the product. He also reported a third compound $\text{Cl}_2 \cdot 7\text{H}_2\text{O}$ and suggested that it consisted of two parts of $\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ and one part of $\text{Cl}_2 \cdot 12\text{H}_2\text{O}$.

Le Chatelier (53) in 1884 studied the decomposition of chlorine hydrate in order to test the principles of thermodynamics and he extended the measurements of the dissociation pressure to include those for the hydrate/ice as well as hydrate/water system. In the same year, Roozeboom (54) studied the conditions of formation, dissociation, composition and density of chlorine hydrate and other hydrates. He dismissed the analyses of previous workers as inaccurate, and analysed large crystals of the hydrate in the hope that they would be less contaminated by mother liquor and less subject to dissociation than smaller crystals. He concluded that

there was only one hydrate, $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$. A year later he also published (48) the temperature dependence of the dissociation pressure of chlorine hydrate in the presence of water or ice.

In 1897 Villard completed a study of the gas hydrates (49) and published his findings in a 105 page article. From his analyses he concluded that chlorine hydrate was $\text{Cl}_2 \cdot 6\text{H}_2\text{O}$. All the hydrates, of both gases and liquids, which he studied formed cubic crystals and had similar other properties. Therefore he stated that the hydrates were a single class of compounds of formula $\text{M} \cdot 6\text{H}_2\text{O}$.

Despite this comprehensive survey of the clathrate hydrates, further researchers continued to study their stoichiometry and properties. In 1901 de Forcrand (55) repeated Le Chatelier's thermochemical experiments to determine the heat of formation of chlorine hydrate from water and chlorine gas and compared the experimental value with the value calculated from the dissociation pressure curves of Isambert, Le Chatelier, and Roozeboom. De Forcrand (56) concluded later that the formula was $\text{Cl}_2 \cdot 7\text{H}_2\text{O}$, and not $\text{Cl}_2 \cdot 6\text{H}_2\text{O}$.

Refinements in the techniques of preparation, drying and analysis were made by Bouzat and Azinières (57) and they concluded in 1923 that the hydrate was $\text{Cl}_2 \cdot 6\text{H}_2\text{O}$, though their results ranged from $\text{Cl}_2 \cdot 6 \cdot 32\text{H}_2\text{O}$ to $\text{Cl}_2 \cdot 6 \cdot 76\text{H}_2\text{O}$. Anwar-Ullah (58), however, was still not

convinced that the stoichiometry was correct and in 1932 he tried three methods of preparation and analysis. He allowed samples to crystallize over different lengths of time, sometimes as long as nine months. In an attempt to prevent any loss of the guest, Anwar-Ullah dried some of the samples in an excess of chlorine. He concluded that the formula was $\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ although his results ranged from 5.9 to 6.45 moles of water per mole of chlorine. It now seemed that finally after 120 years the stoichiometry of chlorine hydrate had been established, but later, X-ray studies were to show that this was not so.

The freezing point of an ethylene oxide/water mixture was first studied in 1919 by Paternò (50). He stated that the hydrate melted at 11°C . In 1922 the stoichiometry of ethylene oxide hydrate was investigated independently by Maass and Boomer (59) and Mazzucchelli and Armenante (60). Maass and Boomer measured the freezing point of mixtures of water and ethylene oxide and found that the temperature/composition curve had a maximum of 10.7°C over the range $\text{C}_2\text{H}_4\text{O} \cdot 0.5\text{H}_2\text{O}$ to $\text{C}_2\text{H}_4\text{O} \cdot 0.8\text{H}_2\text{O}$. They predicted that the stoichiometry of ethylene oxide hydrate was $\text{C}_2\text{H}_4\text{O} \cdot 0.6\text{H}_2\text{O}$. Mazzucchelli and Armenante (60) measured the melting point of frozen solutions in an attempt to avoid supersaturation effects. They observed a break in the temperature/composition curve at about 13 mole % of ethylene oxide in water and about 12.5°C

but the data were not sharp enough to differentiate between 6 and 7 moles of water per mole of ethylene oxide. They also observed that a 1:7 mixture solidified with no excess liquid while a 1:6 mixture crystallized with excess liquid and concluded that the hydrate was $C_2H_4O \cdot 0.7H_2O$.

In 1940 Nikitin (61) proposed that an inclusion compound was formed between water and the second component. This suggestion was confirmed by von Stackelberg (62) in 1947 who studied X-ray powder photographs of some clathrate hydrates and showed them to be clathrates. His incorrect structure gave a stoichiometry of $M \cdot 6H_2O$ (63 - 66). Studies by Claussen (67 - 68) on the space filling properties of pentagonal dodecahedra, and further powder X-ray diffraction experiments by von Stackelberg and co-workers (69 - 76) and by Pauling and Marsh (77) finally showed that these clathrates contained forty-six water molecules in each unit cell and had an ideal stoichiometry of $M \cdot 5.75H_2O$. However, in order to explain the results of Maass and Boomer (59), von Stackelberg and Meuthen (70) assumed that the ethylene oxide molecules only occupied some of the cages.

In 1964 Glew (78) proposed that the oxygen atoms of the ethylene oxide molecules might be incorporated in the host lattice thereby replacing some of the water molecules. This hypothesis does not agree with the

results of dielectric measurements by Davidson and Wilson (79), Davidson, Davies and Williams (80) or with the results of single crystal X-ray studies by McMullan and Jeffrey (81), and has since been abandoned (82). From their X-ray and density measurements McMullan and Jeffrey (81) showed that the stoichiometry of their sample (crystallized from an 8 mole % solution of ethylene oxide in water) was $6.4\text{C}_2\text{H}_4\text{O} \cdot 0.46\text{H}_2\text{O}$. Glew and Rath (82) used a flotation technique to determine the density of the hydrate. By assuming that the unit cell parameters do not change with guest occupancy in the samples studied, they were able to determine the stoichiometries of the crystals. They found a range of values from $6.38\text{C}_2\text{H}_4\text{O} \cdot 0.46\text{H}_2\text{O}$ ($\text{C}_2\text{H}_4\text{O} \cdot 0.7 \cdot 21\text{H}_2\text{O}$) to $6.80\text{C}_2\text{H}_4\text{O} \cdot 0.46\text{H}_2\text{O}$ ($\text{C}_2\text{H}_4\text{O} \cdot 0.6 \cdot 76\text{H}_2\text{O}$) for samples grown under equilibrium conditions from solutions with compositions in the range 3.6 to 13 mole % of ethylene oxide. Glew and Rath also noted that the composition of the crystals varied slightly with the temperature of formation.

McIntyre and Petersen (83) in 1967 studied flash frozen samples prepared from solutions in the composition range $1.08\text{C}_2\text{H}_4\text{O} \cdot 0.46\text{H}_2\text{O}$ to $6.15\text{C}_2\text{H}_4\text{O} \cdot 0.46\text{H}_2\text{O}$ and found that the dimensions of the unit cell increased with increasing concentration of ethylene oxide and with increasing temperature. However, by extrapolation of their results, the change in unit cell dimensions over the range

$6.38\text{C}_2\text{H}_4\text{O} \cdot 0.46\text{H}_2\text{O}$ to $6.80\text{C}_2\text{H}_4\text{O} \cdot 0.46\text{H}_2\text{O}$ is so small that it does not invalidate Glew and Rath's conclusions.

Chlorine hydrate; ethylene oxide hydrate and many other hydrates can have varying occupancy of the cages by the guest within certain limits of stability (84) and are therefore non-stoichiometric.

1.3 Guest Molecules in the Clathrate Hydrates.

Clathrate hydrates are formed by a wide range of guests which include inert gases, hydrocarbons, acidogenic gases and polar and non-polar molecules (62). It is not a criterion for clathrate formation that the guest be a gas, since liquids (49), and solids, such as the tetra-n-butyl ammonium compounds (85), form clathrate hydrates. Von Stackelberg and co-workers (62 - 66, 69 - 76) divided hydrates into two classes, on the basis of whether the guest was a gas or liquid at room temperature, but these divisions were made from a practical and not a theoretical point of view (65). This classification is rarely used today, but the terms liquid hydrate and particularly gas hydrate are used.

Using the chemical nature of the guest molecule Jeffrey and McMullan (40) have classified the clathrate hydrates, into four categories:

a) Hydrophobic compounds which are gases or liquids at 0°C and are only slightly soluble in water. Clathrate formation then gives rise to a 'solubility'

in the solid state that is orders of magnitude greater than found in the liquid state. Guest molecules include methyl chloride, argon, isobutane, and sulphur hexafluoride.

b) Water-soluble acidogenic gases for which clathration is competitive, under the appropriate conditions, with a hydrolytic reaction leading to the formation of ions. Guest molecules include carbon dioxide and sulphur dioxide, but not ammonia or hydrogen chloride, for which the hydrolytic reaction is energetically more favorable.

c) Water-soluble polar compounds with acceptor, or donor and acceptor, hydrogen bonding potential. These have a solubility in water which characteristically increases with a decrease in temperature. Guest molecules include ethylene oxide, dimethylamine, tetrahydrofuran and hexamethylenetetramine. The latter hydrate is unusual in that the guest is totally hydrogen bonded to the water lattice.

d) Water-soluble ternary or quaternary alkylonium salts. In these clathrates the guests are the cations, whilst the anions form part of the hydrogen bonded host lattice. In certain cases, such as a benzoate, the anion may function both as part of the host and as guest. This class differs from the former three in that the interaction between host and guest is that

of a cation within an ionic lattice rather than that of a neutral molecule in a lattice. Nevertheless, this does not necessarily change the nature of the host structure. Guest molecules include $(n\text{-C}_4\text{H}_9)_3\text{S}^+\text{F}^-$, $(\text{iso C}_5\text{H}_{11})_4\text{N}^+$ cation with F^- , Cl^- , OH^- , CrO_4^{2-} , WO_4^{2-} , $\text{C}_6\text{H}_5\text{CO}^-$, or HCO_2^- , anions, and HPF_6 , where the PF_6^- ion is the guest.

In 1897 Villard (49) noted that the clathrate hydrates were sometimes formed by two different guest molecules, particularly by a liquid in the presence of a gas. For example carbon tetrachloride alone does not form a clathrate hydrate but, in the presence of small quantities of air, a stable clathrate is formed (62). Von Stackelberg divided these 'two guest clathrate hydrates' into two classes (62, 76): mixed hydrates (72), and double hydrates (73). When a mixed hydrate is subjected to intermittent pumping at constant temperature the pressure gradually decreases, whereas under the same conditions, a double hydrate creates a constant pressure until completely decomposed (86). Van der Waals and Platteeuw (86, 87) studied ternary systems including the $\text{H}_2\text{S}-\text{C}_3\text{H}_8-\text{H}_2\text{O}$ system and from their results they concluded that von Stackelberg's distinction between double and mixed hydrates was not an essential one. Both types of hydrate are solid solutions of two volatile solutes in a hydrate lattice. Double and mixed

hydrates are therefore similar to other clathrate hydrates and differ only in the fact that they have two guest species rather than one. The reason why some molecules only form hydrates in the presence of a second guest species, often termed a help gas, 'Hilfsgase' of von Stackelberg (62), will be understood when the structures of the clathrate hydrates have been discussed.

1.4 Clathrate Hydrate Structures.

Von Stackelberg and co-workers (62) were the first to propose a structure for chlorine and related clathrate hydrates. They compared the X-ray powder photographs of several hydrates with those of a group of metal borides which they had previously studied (88, 89). The X-ray photographs of the hydrate were lost during the war and so complete structural analyses were not carried out until several years later (69). In this (62) and several later papers (63, 66) they concluded, incorrectly, that the borides and clathrate hydrates were isostructural, and stated that there were forty-eight water molecules and eight identical cages in each unit cell. This gave a stoichiometry, assuming complete occupancy of all the cages, of $M.6H_2O$.

Claussen (67, 68) used the idea of a regular pentagonal dodecahedral arrangement of water molecules and investigated different stacking arrangements for

these units. His results indicated two structural possibilities. The first (67) has large hexakaidecahedral cages together with the smaller pentagonal dodecahedral cages, whilst the second (68) has tetrakaidecahedral cages of an intermediate size together with the pentagonal dodecahedral cages.

Pauling and Marsh (77) carried out a careful X-ray study of chlorine hydrate in 1951 and found that there were only forty-six water molecules and eight cages per unit cell. This structure is identical to Claussen's second structure (68). About the same time von Stackelberg and co-workers studied the hydrates of chlorine, sulphur dioxide, methyl chloride, and hydrogen sulphide, and independently discovered this new and correct structure (69), which they later named Structure I (70). Claussen's first structure (67) was called Structure II. Recently hydrates containing pentakaidecahedra (fifteen faces) and polyhedra with up to sixty faces have been discovered (40) but the vast majority of hydrates of categories (a), (b), (c) in section 1.3 are either Structure I or II and only these structures will be discussed in this thesis.

Structure I hydrates are formed by ethylene oxide, chlorine, and many other small molecules. The $12\text{\AA}$ cubic unit cell, space group $\text{Pm}\bar{3}\text{n}$, O_h^3 , consists of forty-six water molecules with the oxygen atoms arranged at the

vertices of six tetrakaidecahedra and two pentagonal dodecahedra, as illustrated by the circles in Figure 1. The smaller dodecahedral cages (Figure 2a) each have twelve five-sided faces whilst the larger tetrakaidecahedra (Figure 2b) each have twelve pentagonal faces, four of which are shared with adjacent dodecahedra, and two hexagonal faces. The former cages enclose almost spherical spaces with a maximum diameter of $4.86\text{\AA}$ whilst the latter have oblate ellipsoidal cavities with principal axes of 9.0 ± 0.2 , 9.0 ± 0.2 , and $6.0\text{\AA}$. The dodecahedra of twenty water molecules are arranged at the corners and in the centre of the cube. The corner dodecahedra are linked together by two additional water molecules to form hexagons, whilst the translationally non-equivalent central dodecahedron is hydrogen bonded both to the corner dodecahedra and also to twelve of the water molecules in the hexagons. Allen has pointed out (90) that this arrangement of water molecules cannot occur without slight distortions of the pentagonal dodecahedra and tetrakaidecahedra from their regular geometric shapes. Further if the size of the freely rotating guest is close to that of the cage then some distortion of the lattice may occur and the cages may only be partially occupied. For ethylene oxide hydrate McMullan and Jeffrey (81) reported a 20% occupancy of the dodecahedra and complete occupancy of the tetrakaideca-

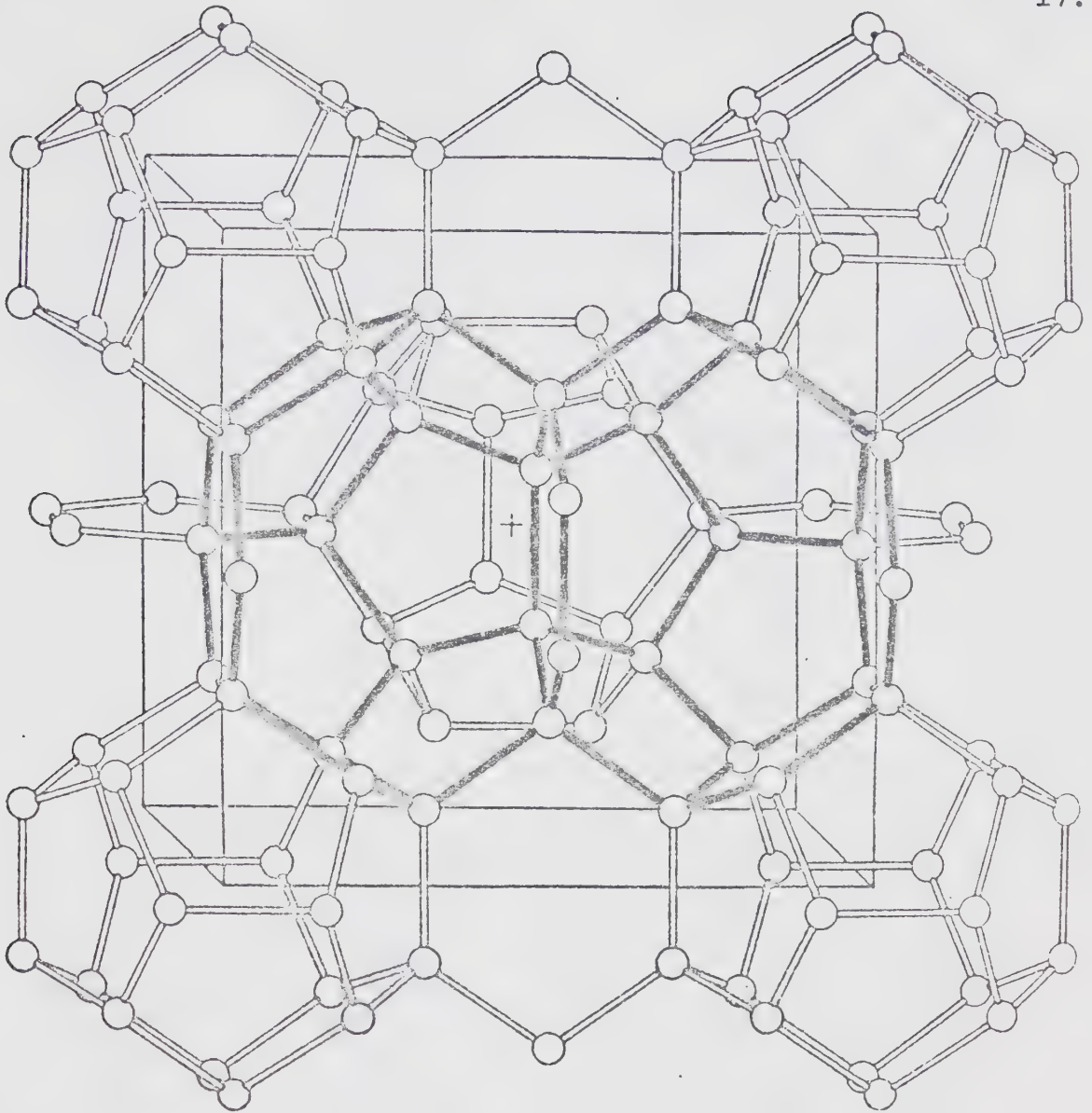


FIGURE 1. The unit cell in a Structure I clathrate hydrate. The circles represent oxygen atoms and the lines represent O-H...O bonds. The darker lines enclose two of the six tetrakaidecahedral cages. Reproduced from reference 81.

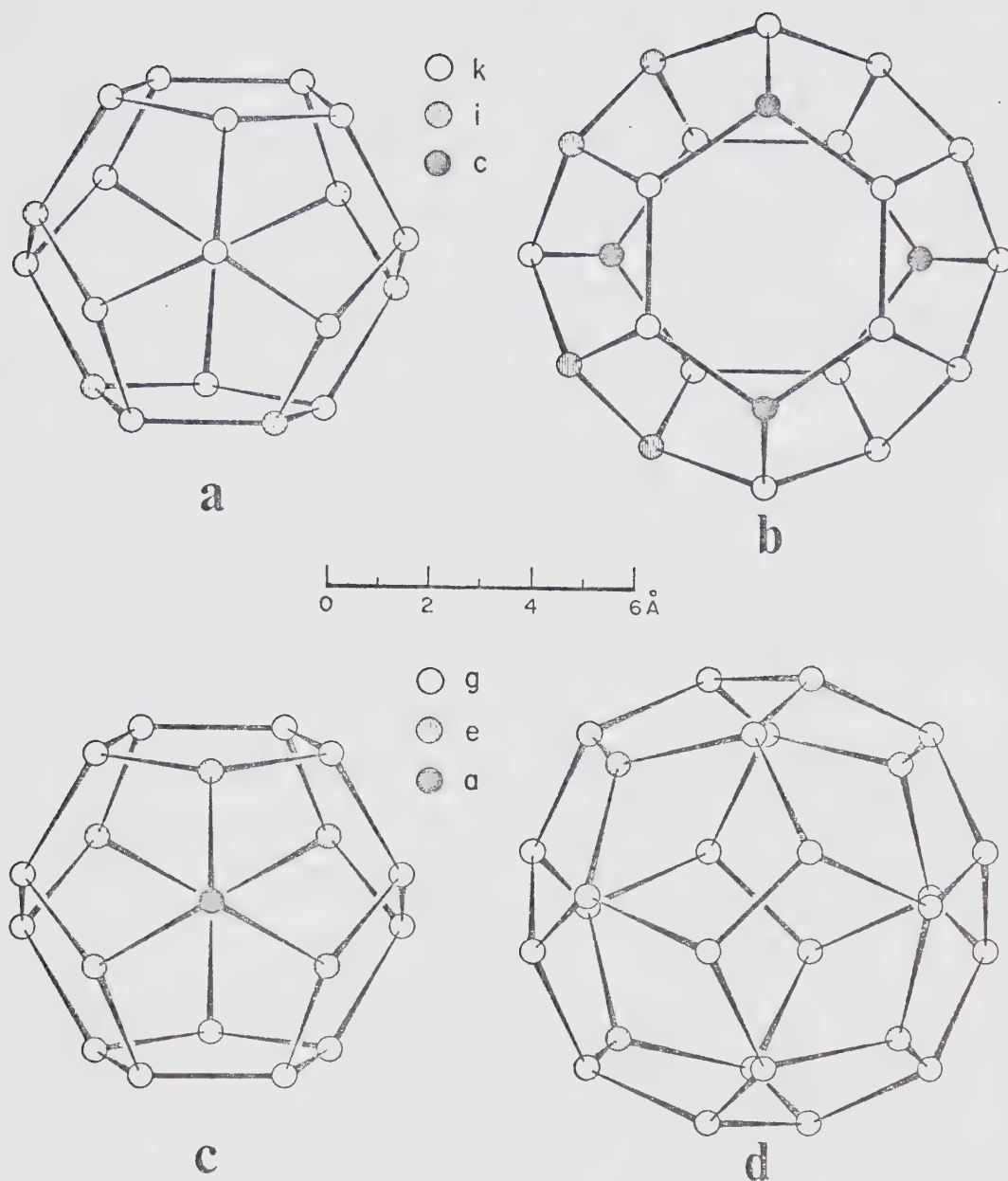


FIGURE 2. Cages of Structure I (a,b) and Structure II (c,d) clathrate hydrates viewed along axes of highest symmetry. Literal identification of the sites follows the notation of The International Tables for X-ray Crystallography. Reproduced from reference 42.

hedra. The O-O bond distances are 2.766, 2.776, 2.811 and 2.844^oÅ at -25°C, and hence there is a slight non-planarity of the pentagons and a distortion of the angles of the planar hexagons. Guests which are too large to fit into the dodecahedra usually form Structure II hydrates.

Structure II hydrates contain pentagonal dodecahedral and hexakaidecahedral cages, the latter being larger than the Structure I tetrakaidecahedra. The 17^oÅ cubic unit cell, space group $Fd\bar{3}m, O_h^7$, consists of one hundred and thirty-six water molecules arranged at the vertices of eight hexakaidecahedra, and sixteen pentagonal dodecahedra, not twelve as Claussen (67) erroneously listed. The pentagonal dodecahedra (Figure 2c) are slightly distorted with two opposite angles tetrahedral. In the lattice the dodecahedra are arranged so that four of them meet at their tetrahedral apices, thereby sharing adjacent faces. This face sharing between pentagonal dodecahedra occurs in three dimensions and the tetrahedral apices form a diamond type lattice. Slightly distorted hexakaidecahedral cages (Figure 2d) are formed in between the dodecahedra. These larger voids each have twelve pentagonal and four hexagonal faces and are almost spherical cavities with a mean diameter of 6.6^oÅ. Mak and McMullan (91) report that the hydrate of tetrahydrofuran and hydrogen sulphide at about -20°C has

O-O bond distances of 2.767, 2.776, 2.796 and 2.812Å^o and slightly non-planar hexagons.

In Structure II hydrates large guest molecules will probably only occupy the hexakaidecahedra, whilst the dodecahedra are empty or are occupied by smaller molecules. For the hydrate of tetrahydrofuran and hydrogen sulphide, Mak and McMullan (91) concluded that the hexakaidecahedra were totally occupied by the tetrahydrofuran molecules but that no tetrahydrofuran occupied the dodecahedra. Instead the pentagonal dodecahedra were 46% occupied by hydrogen sulphide molecules whilst the remainder of these cages were empty. In carbon tetrachloride hydrate von Stackelberg (62) reported that only 0.015 moles of nitrogen and 0.015 moles of oxygen per mole of carbon tetrachloride are needed to stabilize the hydrate. Presumably the oxygen and nitrogen molecules occupy some of the dodecahedra. Unless specific precautions are taken to exclude air during formation it will probably be incorporated into the hydrate. Von Stackelberg (63) has observed the liberation of 'air' from bromine hydrate during its decomposition and found that the 'air' was 50% oxygen and 50% nitrogen.

The stability of many gas hydrates can be increased by raising the pressure of the help gas, as noted by Villard (49). This phenomenon was further investigated by Barrer and co-workers (92 - 95) who studied the

formation of chloroform hydrate in the presence of hydrogen, neon, argon, oxygen, methane, krypton, xenon, ethene, ethane, or carbon dioxide at a pressure of about 700mm of mercury pressure. The hydrates contained chloroform in 94% to 98% of the large cavities but only 0.46% to 64% of the smaller cavities were filled by the help gas. Higher occupancy of the smaller cavities was obtained for spherical gases with a radius similar to that of the pentagonal dodecahedra, for example xenon. Barrer and co-workers (92 - 95) extended their studies to the inclusion of rare gases in Structure I hydrates and from their measurements on both types of hydrates they estimated heats of intercalation and compared these with theoretical models. In this way they were able to explain qualitatively, though not quantitatively, the enhanced stabilization of the hydrates caused by the help gases.

Hence it is now clear why the chemical and many of the physical properties of the guest molecules do not appreciably affect their ability to form gas hydrates. The most important criteria for clathrate hydrate formation are the size and shape of the guest, both of which should be close to those of the cavity. This structural phenomenon of enclathration unites the clathrate hydrates and separates them from all other compounds which crystallize with water of crystallization.

1.5 Occurrence and Uses of Clathrate Hydrates.

The formation of 'snow' in natural gas pipelines at low temperatures and high pressures has caused constriction and sometimes total blockage of the pipe (96, 97). In 1934 Hammerschmidt (96) discovered that a compressed mixture of natural gas and water vapour froze above 0°C. He realized that the solid was either a mixed hydrate, or mixture of hydrates of methane, ethane, propane, and isobutane. Hammerschmidt found that the 'snow' forms most readily at high gas flow rates and melts at 34°F at 110 lbs per square inch, but the melting point increases to 60°F at 800 lbs per square inch. The clathrate hydrate may be destroyed by adding a hydrophilic substance which does not form a hydrate under the ambient conditions (97). Amongst the chemicals which have been used are ammonia, for gases with low carbon dioxide concentrations, and the low molecular weight alcohols (97 - 99). Prevention of hydrate formation is obviously preferable. For this reason, small quantities of ammonia or alcohol are often added to the natural gas or alternatively the gas may be dried, either by means of a drying agent or by refrigeration, until the vapour pressure of the water is below the dew point (96 - 101).

Miller (102) has proposed that clathrate hydrates containing oxygen/nitrogen mixtures may exist at depths greater than 1500 feet below the antarctic ice cap.

Laboratory studies have shown that an oxygen/nitrogen hydrate would be stable at -29°C and 70 bars, the conditions existing at this depth in the ice cap. Its presence would explain the observation that even though gas is evolved on melting deep ice, no bubbles are observed in it.

Speculation on the natural occurrence of clathrate hydrates has not been confined to terrestrial locations. Several laboratory studies on condensed phases (103 - 106) of mixtures of water vapour and guest molecules have been carried out in an attempt to explain some of the physical measurements made on other planets, on comets, and on interstellar particles. Delsemme and Swings (103) have suggested that both the vapour pressures and the rates of sublimation of methane and carbon dioxide clathrate hydrates are of the same order as those observed for the nuclei of comets and for interstellar grains. They suggest that this evidence, together with spectral identification of radicals and ions formed from carbon dioxide and methane, indicates that the CO_2 and CH_4 clathrate hydrates may exist in these environments. On the basis of dissociation pressure measurements, thermodynamic calculations, and a knowledge of planetary environments, Miller (104) proposed that clathrate hydrates should exist in the atmospheres of several planets. He suggested that methane hydrate or a mixed

hydrocarbon hydrate is present on Uranus, Neptune and the satellites and rings of Saturn, and may possibly be present on Saturn, Jupiter and the satellites of Jupiter. Miller also suggested that clathrate hydrates might exist in the atmospheres of Venus and Mars, the Martian ice cap, and even in the high clouds of the earth.

As a result of space exploration further data are being obtained on planetary environments. The Mariner space probes have sent back data on the surface temperature (153°K) of the Martian ice cap and on the partial pressure of carbon dioxide (6.5mb) in the atmosphere, and Miller (105) states that carbon dioxide hydrate can form under these conditions. He notes that the amount of water vapour is insufficient for extensive occurrence of carbon dioxide hydrate in the Martian atmosphere.

Neubager and co-workers (107) report that the temperature measured by Mariner 7 over the frost covered area of the southern cap is 148°K , but they only conclude that this provides evidence that frozen carbon dioxide is its major constituent. Belief in the existence of water molecules on Mars has been encouraged by recent observations.

Using terrestrial observations, McCord and Westphal (108) have observed infra-red absorption features, which differ between light and dark areas of the Martian surface, and which occur in the relative reflection spectra near the expected frequencies for ice and water. Further, the

most recent Mariner photographs (109) show a channel with tributaries which could possibly be caused by water erosion, and also indicate two white spots in a crater close to the Martian equator, where the surface temperature is believed to be too high for solid carbon dioxide to exist.

Clathrate hydrates have also been studied by several commercial enterprises in attempts to find a cheap method of desalinating sea water. Much of this research has not been published or has only been described in patents (110) or technical government reports (111). A brief review of the use of clathrate hydrates in desalination has been given by Bhatnagar (112). The hydrate is usually formed by low molecular weight hydrocarbons at pressures of 30 to 40 atmospheres and about 15°C, so as to minimize the refrigeration costs. When the hydrate is formed from a saline solution the product is salt free. The solid is filtered off and gently warmed, at a lower pressure, until the crystals melt and the hydrocarbon separates out from the pure water as an immiscible liquid. Several pilot plants for desalinating sea water have been built, but the economics of this process may prevent it from being widely used.

Hence clathrate hydrates are believed to occur widely throughout the universe and may increase in practical importance if the costs of water desalination

via clathrate formation can be reduced.

1.6 Studies on the Molecular Dynamics of Clathrate Hydrates.

In the last fifteen years several techniques have been used to study the clathrate hydrates. Dielectric measurements (42, 79, 80, 113 - 125) have yielded information about the relaxation of the water molecules, about the guest reorientation and about the activation energies. Nuclear magnetic resonance studies (42, 117, 121, 122, 125 - 129) have raised the possibility of water molecule or proton diffusion close to the melting point and have characterized the guest motions, whilst X-ray diffraction (40, 42) and theoretical calculations (130) have given evidence about the configurations of the guest in the cage. Limited spectroscopic studies have also been published (131 - 136). The main emphasis in this section will be on the results obtained for ethylene oxide hydrate.

1.6.1 Dielectric Relaxation Studies.

By measuring the dielectric loss ϵ'' or the conductivity σ , dielectric relaxation experiments study the absorption of electrical energy due to the reorientation of polar molecules, and the concomitant change in the dielectric permittivity or dielectric constant, ϵ' . This absorption causes both the orientation polarization and the change in dielectric permittivity, and they are

directly related to its magnitude. The energy absorption and hence the molecular reorientation usually occurs at frequencies below 30Gc/s (1cm^{-1}).

The molecular reorientation is a relaxation or rate process which can be described by either the Arrhenius rate equation or by the Eyring transition state theory. Reorientation can only occur if there are two or more possible orientations with equivalent energies, and obviously, the rate of relaxation is dependent on the local intermolecular forces. Several mechanisms of relaxation have been proposed (115).

For the hydrates, two relaxation processes are generally observed: one at low frequencies, associated with the relaxation of the water molecules, and one at very high frequencies, associated with the relaxation of the guest molecules. The observation of a relaxation phenomenon for the water molecules of the hydrate clearly indicates that the water molecules are disordered, since an ordered solid would show little or no relaxation, as is the case for ice II (137).

The relaxation rates of the water molecules in Structure II hydrates at -40°C are in the range 200c/s to 330Kc/s (123) as compared with values of 150 (138) and 100c/s (139) for ice Ih at -40°C . The water molecules in Structure I hydrates relax even faster than those in Structure II hydrates. For the following hydrates the

values at -40°C are: cyclopropane 530c/s (121), ethylene oxide 480Kc/s (125), nitrogen 800c/s (120), while trimethylene oxide Structure I hydrate relaxes twenty times more rapidly than its Structure II hydrate (114). Hence, although the water molecules in ice Ih and in the Structure I and II clathrate hydrates are tetrahedrally surrounded by other water molecules, the presence of the cages and guest molecules makes the relaxation of the water molecules more facile at these temperatures. The reason for this faster relaxation is not clearly understood but it must involve the number of lattice defects, the energy of defect formation, and the ease of defect propagation. However, the results on hexamethylene-tetramine hydrate, in which there is an activation energy of about two-thirds that in ice, have been tentatively interpreted (118) in terms of an easier propagation mechanism in that hydrate, as compared to ice.

The relaxation of the guest molecules has only been observed in a few hydrates because, at convenient temperatures, it occurs at very high frequencies where experimental techniques are more difficult. Davies and Williams (119) have studied the high frequency relaxation of the guests ethylene oxide, tetrahydrofuran and acetone. Their results indicate that the relaxation rates at 88°K are about: $6.6 \times 10^9 \text{ c/s}$, $1.4 \times 10^{10} \text{ c/s}$, and $3.7 \times 10^{10} \text{ c/s}$ respectively, but the frequency of maximum absorption was not well characterized in their experiments. The

slower relaxation time of the Structure I ethylene oxide hydrate compared with the Structure II tetrahydrofuran and acetone hydrates is attributed (119) to the greater restriction of the ethylene oxide molecule within the tetrakaidecahedron.

The guest molecule relaxation in some hydrates has been studied by Davidson and co-workers (123) down to about 2°K and it was found that a reorientation rate of 1Kc/s occurs for cyclobutanone guest (Structure II) at 31.8°K, for trimethylene oxide guest in its Structure I hydrate at 51.9°K and for ethylene oxide guest (Structure I) at 28.8°K. Cyclobutanone, trimethylene oxide (Structure I) and ethylene oxide are close to the maximum possible guest sizes for the respective hydrate classes and hence their rotation might be expected to slow down at a temperature higher than would be the case for other hydrates. Davidson (42) has confirmed this with observations on other Structure II hydrates where the temperatures associated with guest reorientation rates of 1Kc/s are: acetone 20.2, tetrahydrofuran 21.6, and trimethylene oxide 12.0°K. Similar effects occur in all these hydrates for reorientation rates between 10c/s and 1Mc/s. Thus the guest molecule relaxation rate decreases with increasing guest size, for a given cage, at a given temperature. Dielectric relaxation studies have yielded no evidence of different guest behaviour

in different types of cage in either Structure I or II hydrates (42).

From the studies of the change in relaxation rates with temperature it is possible to calculate the activation energies for reorientation of the guest molecules at these low temperatures (below 40°K). The closer the molecular size is to the size of the cage the higher the activation energy. Ethylene oxide hydrate has an activation energy of 1.42Kcal/mole. For Structure II hydrates the values are: trimethylene oxide 0.60, acetone 1.08, tetrahydrofuran 1.06 and cyclobutanone 1.44Kcal/mole (42). These values are similar to those obtained at higher temperatures by Davies and Williams at Aberystwyth (119), and give average values over the temperature range 30 to 100°K of: 1.26 for ethylene oxide hydrate, 0.82 to 0.94 for acetone hydrate and 0.92Kcal/mole for tetrahydrofuran hydrate (42).

Hence dielectric relaxation studies indicate that the hydrogen atoms of the water molecules are disordered in the hydrates, that the water molecule relaxation slows down until it is undetectable at 100°K, and that the guest molecules do not stop reorienting until very low temperatures. It can also be concluded that, because of this reorientational freedom, only weak interaction exists between host and guest molecules. There is no evidence to suggest that there are large differences

in energy between various orientations of the guest within the cage or within the two types of cage in either Structure I or II hydrate.

1.6.2 Dielectric Constant Measurements.

The dielectric constant at frequencies below about 10^{10} c/s contains contributions from the electronic and atomic polarizations and from those orientation polarizations which arise from frequencies higher than the measurement frequency.

Ice, at -0.1°C , has the low- and high- frequency dielectric constants $\epsilon_0 = 91.5$ and $\epsilon_{\infty} = 3.10$ respectively (138), but as the temperature is lowered the orientation polarization becomes progressively slower and at 100°K no relaxation of the water molecules can be detected (139). At this temperature it is only possible to measure ϵ_{∞} which is between 3.1 and 3.2 (140). The Structure I hydrates of the non-polar molecules, argon (120), nitrogen (120), and cyclopropane (121) have ϵ_{∞} values of 2.85 ± 0.10 . Ethylene oxide hydrate has $\epsilon_0 = 78$ and $\epsilon_{\infty 1} = 10$ at 213°K (125) and at 80°K $\epsilon_{\infty 1}$ can be measured at 1Kc/s and is 14 (125). ϵ_0 is mainly due to the orientation polarization of the water molecules while $\epsilon_{\infty 1}$ is mainly due to the orientation polarization of the guest molecules. At 4°K the guest, ethylene oxide, reorientation rate is less than 1Kc/s (125) and the dielectric constant at 1Kc/s , $\epsilon_{\infty 2} = 4.1 \pm 0.3$. Clathrates of other polar guest molecules

also have $\epsilon_{\infty 2}$ values at 4°K which are considerably higher^{32.} than $\epsilon_{\infty} = 2.85$ observed for hydrates of non-polar molecules (120, 121). This difference is attributed to the atomic polarization, arising mainly from the rotational vibrations of the polar guests, which should absorb light below 100cm^{-1} .

Hence studies of the dielectric constants indicate that hydrates containing polar guest molecules should show quite strong far infra-red absorption by inter-molecular vibrations of the guest molecules (42).

1.6.3 Nuclear Magnetic Resonance Experiments.

Nuclear magnetic resonance studies can give information about the motion of the host water molecules, and of the guest molecules if they contain magnetic nuclei. The most commonly studied magnetic nuclei in the clathrate hydrates are ^1H and ^{19}F (117, 121, 125). Temperature studies are carried out to ascertain the change in molecular motion with temperature (117).

The width of the resonance line is sensitive to the motion of the molecule in which the magnetic nucleus causing the resonance line is situated. However, since the lineshape changes as the rate of molecular motion changes, the second moment of the resonance line is often studied in preference to the linewidth (141). Qualitatively, the second moment is a measure of both linewidth and lineshape. Molecules in a rigid lattice exhibit a broad

resonance line and hence have a large second moment, while rapidly moving molecules are associated with a narrow resonance line and hence have a small second moment (141). The observed second moment can be related qualitatively to the rate of molecular motion provided that the rigid lattice second moment is known or can be estimated from the crystal geometry (42, 125). Activation energies have been calculated from these data (117, 121) but in general they are less accurate than those obtained from dielectric relaxation measurements and, therefore, will not be considered further.

Narrowing of the water proton resonance line of sulphur hexafluoride hydrate (121) and of cyclopropane hydrate (122) is believed by Majid, Garg and Davidson to be caused by the diffusion of water molecules. They suggest (121, 122) that, since this narrowing occurs at a lower temperature in hexagonal ice, the diffusion of water molecules must occur via an interstitial mechanism. Davidson, in a more recent publication (42), suggest that water molecule or at least proton diffusion may be more effective than reorientation in causing line narrowing in clathrate hydrates. However, he points out (42, 142) that the mechanism or mechanisms of diffusion are not yet fully understood.

The behaviour of the guest molecule is usually studied by observing the clathrate deuterates, although

at suitable temperatures two proton resonance lines can be observed for some hydrates. One of these lines is broad and arises from the water, whilst the other is sharp and arises from the guest (122). Brownstein, Davidson and Fiat (117) concluded from a study of the linewidths of several hydrates, including ethylene oxide hydrate, that, down to about -70°C , the guest molecules in both Structure I and II hydrates were rotating rapidly.

For sulphur hexafluoride hydrate, Majid, Garg and Davidson (121) found that the ^{19}F second moment was in agreement with that calculated for an isotropically rotating guest molecule even at -180°C . Similarly for cyclopropane hydrate they also found (122) that at -196°C the second moment of the narrow proton resonance line associated with the guest showed that the cyclopropane molecules were executing rapid, effectively isotropic rotation within their cages. Khanzada and McDowell (129), from their measurements on cyclopropane deuterate, found values of the second moment which are higher by a factor of four than those of Majid, Garg and Davidson, and they concluded that at 77°K the cyclopropane molecule is stationary. By 240°K they say that the molecules are freely rotating about their C_3 axes. Davidson (42) has suggested that the difference between his and Khanzada and McDowell's

results may be attributed to inadequate hydrate content in the samples used by the latter researchers, or by faulty second moment calculations (142). McDowell and Raghunathan (128) have studied the proton magnetic resonance of propane in its clathrate deuterate at temperatures down to about 80°K. Close to the melting point of the clathrate they suggest that the propane undergoes a motional transition from random tumbling to lattice diffusion, whilst below 160°K the propane reorients about its C_2 axis together with methyl group rotations. The second moments observed by these researchers are higher than those observed by Davidson and co-workers for other clathrates and the differences may be due to reasons already mentioned (42, 142).

Ethylene oxide deuterate has been studied by Afanas'ev, Kvividze and Malenkov (127) down to 77°K and down to 2°K by Garg, Morris and Davidson (125) who also studied the hydrate down to about 100°K (125). The results of the two research teams agree reasonably well but a narrow component observed by Afanas'ev above 200°K was not observed by Davidson, who suggests that this may have been caused by some liquid in Afanas'ev's sample. The second moment for ethylene oxide deuterate between 230 and 270°K agrees well with that calculated for isotropic rotation of both guest and host. Between 130 and 200°K the second moment increases slightly and Garg,

Morris and Davidson suggest that this must be caused by incomplete averaging of the intraguest contribution. Below 100°K the second moment rises steadily until at about 5°K, it attains the rigid lattice value calculated using the inter - CH₂ proton separation given by microwave spectroscopy (143). Garg, Morris and Davidson (125) suggest that there is great variability in the reorientational freedom of ethylene oxide molecules in different cages, probably caused by the variable electrostatic fields of the orientationally disordered water molecules of the cages. They have no evidence for different behaviour by the guest in different types of cages.

1.6.4 X-ray Diffraction Studies.

In ethylene oxide hydrate, at -25°C, McMullan and Jeffrey (81) found the four different O-O bond distances of 2.766, 2.776, 2.811 and 2.844 Å to occur in the ratio 2:12:6:3 respectively. They also observed that there was slight distortion of the Structure I cages from the regular geometric shapes. Detailed refinement of the X-ray structure indicated hydrogen atoms in positions of two-fold disorder between each pair of oxygen atoms in the water framework. The tetrakaidecahedra were found to be fully occupied and the distribution of electron density of the ethylene oxide molecules within the cage was explained in terms of two equivalent, but mutually exclusive orientations, as shown in Figure 3, together

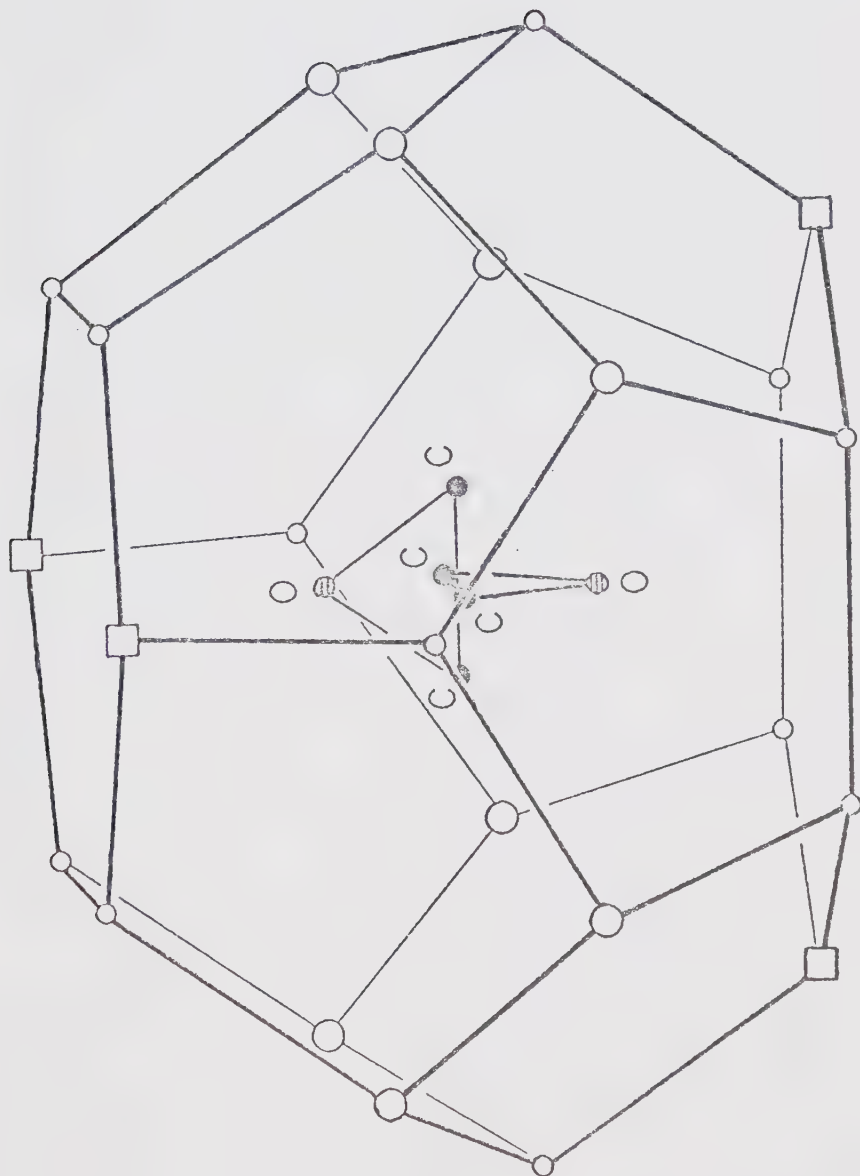


FIGURE 3. The two equilibrium configurations of the ethylene oxide molecule in the tetrakaidecahedral cages suggested from X-ray results. Reproduced from reference 125.

with two average positions which approximated the movement of the ethylene oxide molecule between the preferred sites. McMullan and Jeffrey concluded from their results that the ethylene oxide molecule in the tetrakaidecahedron behaves as a hindered axial rotor, executing motion about its C-C bond and about its two-fold axis, but probably not about the third orthogonal direction perpendicular to the plane of the molecule. Hence, they say that, during transitions between the two preferred orientations, the methylene groups would remain near the circular plane of 9 Å diameter and the oxygen atoms would further populate this plane of minimum potential energy at the expense of a position closer to the hexagonal faces. The dielectric relaxation studies (79, 80, 119, 125), nuclear magnetic resonance studies (117, 125, 127) and calculations on the energy of different orientations in the tetrakaidecahedron (130) do not support these conclusions.

McMullan and Jeffrey (81) were also able to conclude, from their refinement of the X-ray structure, that 20% of the pentagonal dodecahedra were occupied by molecules which were highly disordered. These were probably ethylene oxide molecules, but could possibly be an impurity guest molecule, freely rotating. In order to explain their density measurements they assumed that no air or other impurity had been incorporated into the sample and that all guest molecules were ethylene oxide.

McIntyre and Petersen (83) have carried out X-ray studies on flash frozen solutions of ethylene oxide in water and have shown that the unit cell contracts on cooling and with decrease in ethylene oxide content. Their unit cell parameters are consistent with the value of $12.03\text{\AA}$ found by McMullan and Jeffrey for $6.4\text{C}_2\text{H}_4\text{O} \cdot 0.46\text{H}_2\text{O}$ at -25°C .

1.6.5 Spectroscopic Measurements.

One study by neutron spectroscopy (131) and five studies by infra-red spectroscopy (132 - 136) on the clathrate hydrates have been reported.

Naumann and Safford (131) carried out inelastic neutron scattering experiments on ice I and sulphur dioxide hydrate at 248°K . No details of sample preparation or characterization are reported but the spectra are similar. In both spectra there is a strong peak at $560 \pm 30\text{cm}^{-1}$, assigned to torsional oscillations, and a broad maximum between 300 and 100cm^{-1} . Below 100cm^{-1} there is a maximum in ice at 49cm^{-1} and in the sulphur dioxide hydrate at 69cm^{-1} . These differences are attributed (131) to small shifts in the low frequency lattice vibrations, caused by small differences in O-O bond distances, or by changes in the weak dispersion forces which stabilize the polyhedral water lattice.

Harvey, McCourt and Shurvell prepared samples for infra-red study (132) by condensing mixtures of sulphur

dioxide and water vapour on a cesium iodide window at 78°K, and then annealing at 110°K. They assumed that the clathrate hydrate of sulphur dioxide was formed. Spectra of hydrogen sulphide and krypton hydrates were also reported. Recently Hardin and Harvey (133) have reported that the probable phase studied, in each case, was an amorphous mixture of ice and guest, and not a clathrate hydrate. Hence none of the spectra will be discussed. Luck and Ditter (134) have published a spectrum of the first overtone OH stretching band, at about 5000cm^{-1} , of ice and uncharacterized sulphur dioxide hydrate and they report an upward shift of 70cm^{-1} for the hydrate.

Studies by Chen (135) of aqueous suspensions of methyl chloride hydrate, prepared by passing methyl chloride through ice cooled water with stirring, indicated that the peaks due to the H_2O vibrations were similar to those in ice. However, because of the presence of water in the samples studied, very little can be concluded about the shape or even the exact frequencies of the hydrate bands.

Falk (136) has studied the infra-red spectra, over a limited range, of liquid and solid trimethylamine hydrate, $(\text{CH}_3)_3\text{N} \cdot 10\frac{1}{4}\text{H}_2\text{O}$, and has concluded that the band profiles of the ν_{OD} (HDO) absorption of dilute HDO in liquid trimethylamine hydrate differ only slightly from

those in liquid water. He concludes that the distribution of hydrogen bond strengths has the same general form in the two media, and the absence of any features in the region expected for ice or solid hydrate indicates the absence of structurally well defined hydrate regions in the liquid phase. His spectra of the $\nu_{OD}(\text{HDO})$ band of ice and hydrate are very similar in frequency of maximum absorption, 2420cm^{-1} , though the centre of gravity of the hydrate band is about 10cm^{-1} higher than that of ice Ih, and the band is broader. Falk concludes that these results are consistent with the crystallographic observation of twelve distinct OH groups having ten distinct O-O bond lengths and two O-N bond distances.

Hence, to date, no wide frequency range infra-red study of reliably characterized samples of clathrate hydrates has been published.

In this chapter the absorption of infra-red radiation by the vibrations in solids is discussed. When a vibrating system of N particles is treated theoretically using the harmonic approximation (144), the potential energy, V , is expressed as:

$$2V = \sum_{i,j=1}^{3N-6} f_{ij} q_i q_j ,$$

and the kinetic energy, T , is expressed as:

$$2T = \sum_{i,j=1}^{3N-6} b_{ij} \dot{q}_i \dot{q}_j ,$$

where q_i and q_j are the displacement coordinates, $\dot{q}_i$ and $\dot{q}_j$ are their time derivatives, and f_{ij} and b_{ij} are constants for given values of i and j . A transformation is then found to the normal coordinates, Q_i , in which the potential energy is given by:

$$2V = \sum_{i=1}^{3N-6} \lambda_i Q_i^2 ,$$

and the kinetic energy by:

$$2T = \sum_{i=1}^{3N-6} \dot{Q}_i^2 ,$$

where $\dot{Q}_i$ denotes the time derivative of Q_i , and λ_i is equal to $4\pi^2 \nu_i^2$, where ν_i is the classical vibration frequency. In terms of the normal coordinates the quantum mechanical treatment of the vibrating system reduces to a study of the simple harmonic oscillator. One simple harmonic oscillator wave equation is obtained for each normal

coordinate, and thus a set of wave functions, $\psi_{v_i}(Q_i)$,^{43.} and of energies, E_i , equal to $(v_i + \frac{1}{2})h\nu_i$, result. The total wave function of the system, Ψ , is given by:

$$\Psi = \prod_{i=1}^{3N-6} \psi_{v_i}(Q_i) ,$$

and the total energy, E , by:

$$E = \sum_{i=1}^{3N-6} E_i .$$

Hence, in the harmonic approximation, the quantum mechanical treatment reduces to the consideration of each normal coordinate independently.

The probability of a vibrational transition is related to (144) the transition moment integral $\int \psi_u^* \underline{\mu} \cdot \psi_l d\tau$, where $\underline{\mu}$ represents the dipole moment of the system, and the subscripts u and l denote upper and lower states, respectively. If the dipole moment is expressed as:

$$\underline{\mu} = \underline{\mu}_0 + \sum_{i=1}^{3N-6} \frac{\partial \underline{\mu}}{\partial Q_i} \cdot Q_i ,$$

then the only allowed transitions are those for which $\Delta v_i = \pm 1$. Further, for any such transitions to be allowed the transition moment integrand must be totally symmetric in the symmetry group of the system. Fundamental transitions occur between the ground state of the system and the state in which just one v_i equals one. The ground vibrational state is totally symmetric; therefore, the upper state wave function and the dipole moment must transform identically under all operations of the symmetry

group if the transition is to be allowed. The symmetry of the $v_i = 1$ state wave function for a simple harmonic oscillator is identical to the symmetry of the normal coordinate. Thus, to discuss qualitatively the absorption of light by fundamental transitions one need not use quantum mechanics, but can use classical mechanics and can talk of classical vibrations, which are understood to mean normal vibrations or normal coordinates. This approach is taken in the following discussion of the absorption of light by ordered and by disordered solids. The discussion is deliberately rather qualitative and general in order to emphasize the main points. Only fundamental absorption is discussed. More complicated absorption such as hot bands, transitions from states in which v_i is not zero, combination bands and overtones are neglected (145).

2.1 Ordered Solids

Infra-red radiation consists of electromagnetic waves which can be regarded as mutually orthogonal electric and magnetic fields, both of which are perpendicular to the direction of propagation of the light wave. Mathematically the electric field, $\underline{E}$, at a point along the direction of propagation at a distance $\underline{l}$ from the origin, and at a time, t , is given by:

$$\underline{E} = \underline{E}_0 \cos(2\pi \underline{K} \cdot \underline{l} - 2\pi ft + \phi).$$

$\underline{K}$ is the wave vector of the light, defined as having the

direction of the light propagation and having magnitude equal to the reciprocal of the wave length of the light, f is the frequency of the light, and ϕ is arbitrary.

Vibrations in ordered crystals can also be regarded as waves whose displacement $\underline{R}_1$ at the point 1 in the crystal at time t is given by:

$$\underline{R}_1 = \underline{R}_0 \cos(2\pi \underline{k} \cdot \underline{1} - 2\pi f' t + \Theta) ,$$

where $\underline{k}$ is the wave vector of the vibration, f' is the frequency of the vibration and Θ is arbitrary. The change, $\underline{\mu}_1$, in the dipole moment at point 1 , associated with this vibration is given by:

$$\underline{\mu}_1 = \underline{\mu}_0 \cos(2\pi \underline{k} \cdot \underline{1} - 2\pi f' t + \Theta) ,$$

where $\underline{k}$, $\underline{1}$, f' , t and Θ have been defined above.

The total interaction energy between the radiation and dipole moment changes, over the entire crystal, W , is given by:

$$W = \underline{E} \cdot \underline{\mu} = \underline{E}_0 \cdot \underline{\mu}_0 \sum_t \sum_1 [\cos(2\pi \underline{K} \cdot \underline{1} - 2\pi f t + \phi) \cdot \cos(2\pi \underline{k} \cdot \underline{1} - 2\pi f' t + \Theta)] .$$

Since ϕ and Θ are arbitrary constants which take account of the phase angle of the wave at time $t = 0$ and position $1 = 0$ we may define Θ as zero and regard ϕ as being determined relative to it. After rearrangement the equation becomes:

$$W = \underline{E}_0 \cdot \underline{\mu}_0 \sum_t \sum_l \left[\frac{\cos \phi}{2} \left\{ \cos 2\pi [\underline{l} \cdot (\underline{K} + \underline{k}) - t(f + f')] \right. \right. \\ \left. \left. + \cos 2\pi [\underline{l} \cdot (\underline{K} - \underline{k}) - t(f - f')] \right\} \right. \\ \left. - \frac{\sin \phi}{2} \left\{ \sin 2\pi [\underline{l} \cdot (\underline{K} + \underline{k}) - t(f + f')] \right. \right. \\ \left. \left. + \sin 2\pi [\underline{l} \cdot (\underline{K} - \underline{k}) - t(f - f')] \right\} \right]. \quad 46.$$

For the sum over all values of l to be non-zero, either $\underline{K} = \underline{k}$ or $\underline{K} = -\underline{k}$; expressing it another way, the two waves must be collinear and have the same wavelength. Similarly, if the sum over all values of t is to be non-zero, then $f = f'$. The solutions $f = f' = 0$, $f = -f'$, and $\underline{K} = \underline{k} = 0$ also exist but have no physical significance. For maximum interaction, the two waves should be in phase, that is to say $\phi = 0$ and $\underline{E}_0 \cdot \underline{\mu}_0 = |\underline{E}_0| |\underline{\mu}_0|$. The selection rule for fundamental infra-red absorption is therefore: the wave vector of the light must equal the wave vector of the vibration or its negative, and the frequencies of the two vibrations must equal one another.

Infra-red radiation has wavelengths between about 2×10^{-4} cm and 10^{-1} cm whereas the dimensions of most unit cells are of the order of 10^{-7} cm. Hence the infra-red active vibrations have wavelengths of at least one thousand unit cell lengths. For crystals in which there are only short range forces, extending over a few unit cells, the frequency of a vibration with a wavelength of the order of 10^{-4} cm is essentially the same as the frequency of a vibration of infinite wavelength.

Therefore the selection rule for infra-red absorption by such crystals effectively reduces to the statement: only zero wave vector vibrations can absorb infra-red light through fundamental transitions. In crystals where there are long range interactions extending over many unit cells, the preceeding simplification does not apply although it is still a very useful first approximation. Strictly, this limitation applies to any infra-red active vibration since the dipole moment change associated with the vibration causes long range interactions in the crystal. In practice effects due to this have only been observed for very strongly absorbing vibrations (146).

When the approximation, $\underline{k} = 0$, is used, it is unnecessary to study the entire space group to predict the infra-red activity of the crystal vibrations. Instead the unit cell group (147) is used to determine the representation formed by the vibrations and hence their infra-red activity. This procedure is often, rather misleadingly, referred to as factor group analysis and this term and the term factor group allowed transitions, are so widely used that they will be adopted in this thesis. The factor group allowed vibrations are the only ones which yield fundamental transitions observable in the infra-red spectrum of an ordered solid, but overtone and combination vibrations, which do not obey the

selection rule $\underline{k} = 0$, are also observed, usually as broad absorptions. Hence, although about 10^{24} vibrations exist per mole of molecules, the number of fundamental infra-red absorption bands is of the order of the number of atoms in the unit cell. More detailed discussions of the absorption of infra-red light by ordered crystals and of factor group analysis can be found in many textbooks, reviews, and papers (147 - 152).

The spectra of many ordered non hydrogen bonded solids have been successfully interpreted using factor group analyses, but the degree of success is much less for hydrogen bonded solids. The most extensive infra-red studies of a non hydrogen bonded, ordered molecular crystal are those on benzene (153 - 163). The space group of solid benzene is $Pbca$, D_{2h}^{15} , and there are four molecules per unit cell, all on centres of inversion (159). Factor group analysis of the translational and rotational displacements of the molecules predicts that six translational vibrations but no rotational vibrations are infra-red active. The observed spectra vary considerably in detail (156, 160, 161, 163) and Harada and Shimanouchi (163) have discussed the results of all these studies and have shown that at least five distinct bands are observed at 100°K.

Factor group analysis of the intramolecular vibrations of solid benzene predicts that each of the

fifteen ungerade vibrations, of the isolated molecule, is split into one infra-red inactive and three infra-red active vibrations. Hence each molecular E_u mode yields six infra-red active crystal modes. Absorption by these factor group components is observed for some molecular vibrations. For example, ν_{11} , the A_{2u} out of plane CH vibration of the isolated molecule causes bands at 706.62 , 681.35 , and 679.7cm^{-1} in the spectrum of the solid (154). However in many cases the band separation is so small that they are not resolvable and hence fewer absorptions are actually observed than are predicted. Factor group analysis predicts the symmetry species of the components of each molecular vibration as A_u , B_{1u} , B_{2u} , B_{3u} , where the A_u component is infra-red inactive. The transition moments for the B_{1u} , B_{2u} , and B_{3u} factor group components are mutually orthogonal, and directed along the crystal axes. Hence studies of single crystals using polarized infra-red radiation can identify the three components. For example, Marzocchi, Bonadeo, and Taddei (162) have shown that the B_{2u} component of the ν_{11} band absorbs at 707.3cm^{-1} whilst the B_{1u} and B_{3u} components absorb at 682 and 681cm^{-1} .

In this way, factor group analysis can be used to interpret the spectra of ordered non hydrogen bonded solids. It can also be used to interpret some features of the spectra of ordered hydrogen bonded solids, but

absorptions by vibrations of hydrogen bonded hydrogen atoms do not obey the factor group selection rules. To illustrate this point, the spectra of the ordered ices and of methanol will be discussed.

X-ray and neutron diffraction studies of the various phases of ice have shown that ice II (164 - 169), ice VIII (169) and ice IX (164*, 169*, 170*, 171*, 172; * indicates that in these references ice IX is called ice III, see page 52) have ordered structures in which the positions of both the oxygen and hydrogen atoms in different unit cells are symmetry related. The translational lattice vibrations in the ices are generally observed below 400cm^{-1} , in the far infra-red region (173), whereas above this frequency, in the mid-infra-red region, absorptions due to the rotational lattice vibrations and intramolecular vibrations are observed (174). The far infra-red spectra of ice II and ice IX have been studied by Bertie, Labbé and Whalley (175) and both show sharp lines, most of which are five to ten wavenumbers in halfwidth. A factor group analysis of the translational vibrations of ice II, space group $R\bar{3}$, S_6^2 , predicts that five A_u and five E_u vibrations should be infra-red active under the point group S_6 , giving a total of ten bands. The far infra-red spectrum (175) shows either nine peaks and shoulders, or ten features, if the drop-off below 100cm^{-1} is regarded as a weak shoulder. Factor group analysis of the translational vibrations of ice IX, space group $P4_12_12$, D_4^4 , predicts twelve infra-

red active bands, four A_2 and eight E, under the point group D_4 . In the far infra-red spectrum (175) only eight absorption maxima are observed. However, at least three of the bands have halfwidths of about 12cm^{-1} , compared with 4 to 9cm^{-1} for the other bands, and it is probable that two or more vibrations contribute to these broader bands.

Hence the far infra-red spectra of the ordered ices, due to absorption by translational lattice vibrations, can be understood in terms of infra-red active factor group allowed transitions. Alternatively a sharp lined spectrum due to absorption by translational lattice vibrations is evidence of an ordered solid.

The rotational vibrations of the water molecules in the ices occur between 400 and 1000cm^{-1} , and lead to an absorption referred to as the ν_R band (176, 177). In ice II fifteen sharp features have been observed in this region for the H_2O ice and ten for the D_2O ice but they are superimposed on an intense broad absorption (177). The entire band shows an isotope shift of about 1.35, and clearly most of the features arise from rotational vibrations. The sharp features have halfwidths comparable to those seen for translational modes (177). The broad peak is apparently associated with the hydrogen bonded proton motions. A factor group analysis of the rotational modes shows that the thirty-six zero wave vector

rotational vibrations form the representation $6A_g + 6A_u + 6E_g + 6E_u$ under the S_6 point group. The six A_u and six E_u bands are infra-red active and Bertie and Whalley concluded that presumably the stronger and sharper features of ν_R are associated with these factor group allowed transitions (175). Eleven sharp features, superimposed on a broad absorption, were observed in the ν_R band of ice IX (177, in this reference ice IX was again called ice III). A factor group analysis of the rotational lattice vibrations of ice IX shows that they form the representation $4A_1 + 5A_2 + 4B_1 + 5B_2 + 9E$ under the point group D_4 . The five A_2 and nine E vibrations are infra-red active. Bertie and Whalley stated that clearly most of the eleven sharp features are to be distributed amongst the fourteen expected fundamentals. The broad band can, once again, only be attributed to the motions of the hydrogen bonded hydrogen atoms.

At the time that these spectroscopic studies were carried out, it was not known that ices II and IX were ordered. The existence of order in the hydrogen atom positions extending over at least a few unit cells was first predicted because these sharp ν_R absorption features decrease in intensity when a few percent of deuterium is introduced into the lattice to create disorder (177). The order in ice II is now established as a result of dielectric relaxation (137), X-ray diffraction (165, 169) and neutron diffraction (167, 168) studies. The early work

on ice IX (164, 169 - 171, 177) was reported as being on ice III. However, Whalley, using dielectric relaxation techniques, observed a change from a disordered to an ordered phase as ice III was cooled, and named the low temperature ordered form, ice IX (178). The existence of order in ice IX has also been shown by neutron diffraction (172) studies.

The intramolecular absorptions in the ices occur at about 1600 and 3200cm^{-1} and have been assigned (176, 177) to the H-O-H angle deformation and the OH stretching vibrations respectively. These bands are several hundred wavenumbers in halfwidth, are rather featureless, and are clearly not explainable by factor group analysis, even in the ordered forms of ice. The vibrations primarily involve motion of a hydrogen bonded hydrogen atom. The reason for the extreme breadth is not clearly understood (176) but is definitely related to the vibrational coupling between molecules.

The spectra of the O-H and O-D stretching modes of the ices can be observed in the absence of this intermolecular coupling by studying 1 to 5% solutions of H_2O in D_2O or vice versa. In 95% D_2O the absorption by the O-H stretching mode of HDO, $\nu_{\text{OH}}(\text{HDO})$, can be studied, while in 95% H_2O $\nu_{\text{OD}}(\text{HDO})$ can be readily seen. These modes are often referred to as the isolated OH or OD stretching modes because, for example, each OH bond is

isolated from other OH bonds by the OD bonds of the solvent. The spectra of ice II show four $\nu_{\text{OD}}(\text{HDO})$ and three $\nu_{\text{OH}}(\text{HDO})$ peaks (177). The peak frequencies, 2493, 2481, 2460 and 2455 for $\nu_{\text{OD}}(\text{HDO})$, can be related to the observed O-O bond lengths of 2.844, 2.803, 2.781 and 2.768 Å at 110°K (168, 171). The plot of peak frequencies against O-O bond lengths is linear with a slope of $510\text{cm}^{-1}/\text{\AA}$ at 2.80 Å (168, 171). The two peaks at 2460 and 2455cm^{-1} are well resolved and, hence, their halfwidths must be less than 5cm^{-1} , which is nearly forty times sharper than the $\nu_{\text{OD}}(\text{D}_2\text{O})$ absorption and clearly illustrates the effect of intermolecular coupling. Similar differences were observed (177) between $\nu_{\text{OH}}(\text{HDO})$ and $\nu_{\text{OH}}(\text{H}_2\text{O})$.

There are peaks at 2461 and 2450cm^{-1} due to $\nu_{\text{OD}}(\text{HDO})$ in the spectrum of ice IX (177). X-ray and neutron diffraction studies of ice IX (171, 172) show that the structure contains O-O bond distances of 2.806, 2.763 and 2.747 Å in the ratio 3:3:2. If the weighted mean of the two shorter bond lengths is plotted against the frequency, 2450cm^{-1} , the point lies on the line for ice II, but the second point does not (171). Nevertheless the $\nu_{\text{OD}}(\text{HDO})$ bands are at least twenty times sharper than those due to $\nu_{\text{OD}}(\text{D}_2\text{O})$, and similar comments apply to the halfwidths of the $\nu_{\text{OH}}(\text{HDO})$ compared with the $\nu_{\text{OH}}(\text{H}_2\text{O})$ bands (177).

Thus, while the absorption by the intramolecular modes of the H_2O and D_2O ices cannot be completely understood, useful information can be obtained from the $\nu_{\text{OH}}(\text{HDO})$ and $\nu_{\text{OD}}(\text{HDO})$ bands observed in dilute isotopic samples. This information can predict or confirm order in an ice phase and can often indicate the number of different O-O bond distances present.

The infra-red spectra of solid methanol and methanol- d_4 have been studied by Falk and Whalley (179) and by Dempster and Zerbi (180). Two solid forms exist, both of which contain hydrogen bonded chains of methanol molecules (181). The spectra contain broad absorptions due to vibrations which primarily involve motion of the hydrogen bonded hydrogen atoms, and sharp absorptions by those vibrations which do not primarily involve these atoms. The sharp absorptions can be discussed in terms of factor group allowed transitions, but clearly the broad absorptions can not be explained in the same way (179, 180).

Hence, hydrogen bonded ordered solids show sharp absorptions due to translational lattice vibrations which can be related to factor group allowed transitions. The absorptions due to rotational lattice vibrations are broad with sharp superimposed features; the sharp features can be assigned to factor group allowed transitions, but the broad band can only be assigned to

effects of the hydrogen bonded hydrogen atom. Intra-molecular absorptions are broad if they are caused by vibrations which mainly involve the motion of hydrogen bonded hydrogen atoms, but otherwise they are sharp and can be related to factor group allowed transitions. By contrast, the absorptions in non hydrogen bonded ordered solids are sharp and can be interpreted using factor group analysis.

2.2 Disordered Solids.

X-ray and neutron diffraction studies have shown that ice Ih (164, 169, 182 - 187), ice Ic (169, 188, 189), ice III (190), ice V (164, 166, 169), ice VI (169, 191 - 193) and ice VII (169, 192 - 194) contain orientationally disordered water molecules, whose arrangements are subject to the Bernal - Fowler rules. Ices V (166, 169) and VI (195) are partially ordered, while the other phases are believed to be totally disordered, apart from short range correlation effects. All of these ice phases have far infra-red spectra which are broad, in contrast to the sharp line spectra of the ordered ices, thus characterizing the phases as being disordered.

These spectral differences between the ordered and disordered ices led Bertie and Whalley (196) to propose a theory for the absorption by translational vibrations of orientationally disordered crystals, in which the

molecules are situated on, or very close to, regular lattice sites, and are oriented randomly. The potential field opposing translation of the molecules clearly shows approximate translational symmetry, otherwise the molecules would not be on, or near to, lattice sites. Hence the translational vibrations in these crystals can be called mechanically regular and can be described by the same wave notation as for ordered crystals (section 2.1). Absorption of infra-red light by such vibrations is due to changes in the dipole moments during translational displacements of the molecules. The dipole moment can be regarded as containing two parts, the permanent dipole moment, and the dipole moment induced in the molecule by the surrounding molecules. It is only this induced part of the dipole moment that changes during a translational lattice vibration. Because the orientation of a molecule on one site in a given unit cell is randomly related to the orientations of molecules on the same site in other unit cells, the principal polarizability axes are also disordered from one cell to the next, and hence the induced dipole moments are disordered. Further, the changes in the induced dipole moments during a translational vibration are disordered. Thus the translational vibrations can be termed electrically irregular. A simple visual understanding of this point can be obtained by considering the dipole moment

change associated with the stretching of an $\text{O}-\text{H}\cdots\text{O}$ bond compared with that for the stretching of an $\text{O}\cdots\text{H}-\text{O}$ bond. The dipole moment changes will be opposite in the two cases. In an orientationally disordered ice phase, equivalent bonds in different unit cells are essentially randomly $\text{O}-\text{H}\cdots\text{O}$ or $\text{O}\cdots\text{H}-\text{O}$ bonds, and hence the dipole moment changes are irregular. It is important to note, however, that the theory is not limited to the assumption that all of the dipole moment change is associated with the individual hydrogen bonds (196).

The change, μ_1 , in the induced dipole moment at a point 1 in an orientationally disordered crystal, during a vibration of wave vector $\underline{k}$ and frequency f , is given by:

$$\mu_1 = \mu_0 \cos(2\pi \underline{k} \cdot \underline{1} - 2\pi f t + \theta),$$

where μ_0 is proportional to the dipole moment derivative with respect to translation of a molecule. μ_0 can be expressed mathematically as the sum of an average part, μ_{av} , where the average is over equivalent molecules and displacements in all unit cells, and a random part, μ_{r1} , which is dependent on the position 1 in the crystal.

Hence:

$$\mu_1 = (\mu_{av} + \mu_{r1}) \cos(2\pi \underline{k} \cdot \underline{1} - 2\pi f t + \theta).$$

The interaction energy between the crystal vibration and the infra-red light wave is only non-zero when summed over time if the frequencies of the two waves are the

same (section 2.1). Further, for maximum interaction, the phase angle between the two waves must again be zero.

Making use of these relationships, the spatial dependence of the interaction energy, W , may be expressed, by analogy with the equation for ordered crystals, as:

$$W = E_0 \sum_l \mu_{av} \cos(2\pi \underline{k} \cdot \underline{l}) \cdot \cos(2\pi \underline{K} \cdot \underline{l}) \\ + E_0 \sum_l \mu_{rl} \cos(2\pi \underline{k} \cdot \underline{l}) \cdot \cos(2\pi \underline{K} \cdot \underline{l}).$$

The first term is analogous to that for ordered crystals and is only non-zero if $\underline{K} = \underline{k}$, whilst the second term has the most probable value of zero, since μ_{rl} is random with respect to position l , over which it is summed.

The total intensity of absorption, I , is proportional to W^2 , the square of the interaction energy. The square of the first sum in the equation is zero unless $\underline{k} = \underline{K}$, yielding the same selection rules from the average part of the dipole moment derivative as for ordered crystals. Thus sharp absorptions due to diffraction factor group allowed transitions may be observed. Cross-terms between terms in the first sum and those in the second sum add to a most probable value of zero, because of the random nature of μ_{rl} with respect to l . The square of the second sum contains two types of terms, those involving $\mu_{rl} \mu_{r'l'}$, which sum to zero because of the randomness in μ_{rl} , and those in $|\mu_{rl}|^2$ which sum to a finite term for all values of the wave vector $\underline{k}$. This contribution, I' , to the intensity from the irregular part of the dipole moment

derivative is given by:

$$I' = E_o^2 \sum_l \mu_{rl}^2 \cos^2(2\pi \underline{k} \cdot \underline{l}) \cdot \cos^2(2\pi \underline{k} \cdot \underline{l}),$$

and no selection rules for $\underline{k}$ exist since the summation over l is non zero for all values of $\underline{k}$. Hence, because of the orientational disorder of the molecules in the crystal, all vibrations are, in principle, infra-red active.

A very simplified analysis, using only one force constant and one dipole moment derivative has shown that the absorption intensity for this model is proportional to f^2 , the square of the vibration frequency (196). Hence the resultant spectrum is expected to depend on the number of translational vibrations at each frequency, the density of states, multiplied by the square of the frequency. However, in the ices the molecular orientations are not completely random and recent work has attempted to allow for this short range correlation (197).

The far infra-red spectra of ice Ih and Ic (198, 199) are identical within experimental error and consist of a broad band stretching from 360cm^{-1} down to at least 17cm^{-1} with a maximum at 229.2cm^{-1} , and other features which may be described as shoulders, dips and points of inflexion. The spectrum of ice Ic has been interpreted (198) using the density of states of diamond, which has the same crystal structure as the oxygen atoms of ice Ic. This interpretation failed to explain the features above

240cm^{-1} which were attributed to the influence of long range forces. No factor group allowed translational lattice vibrations are either predicted or observed. Ice Ih is presumed, because of its spectral similarity to ice Ic, to have a similar density of states.

Of the other ice phases containing orientationally disordered water molecules, only ices V and VI have been studied by infra-red spectroscopy (175, 200). Both have broad and relatively featureless far infra-red spectra with maxima at 200 and 187cm^{-1} respectively. The absorption is, again, due to translational vibrations and is often referred to as the ν_T absorption. The interpretation of the broad absorption is believed to follow that of the spectra of ice I, but unfortunately the frequency/wavevector dispersion curves, and the density of states curves are not known for these phases and hence a detailed interpretation is impossible.

In ice V sharp features are observed at 146 , 126 and 95cm^{-1} and these were originally assigned to some of the diffraction factor group allowed transitions (175). Since that time ice V has been shown to be partially ordered (166, 169) and Solinas (201) has suggested that the sharp lines in the spectra appear because of this partial order. Ice VI does not show any such sharp lines (200), and it has recently also been shown to be partially ordered (195). The significance of this result

cannot be evaluated until the detailed structure is available. Hexamethylenetetramine hydrate is also partly ordered (118), and its far infra-red spectrum mainly consists of sharp line absorptions, the number of features agreeing with that predicted from the diffraction factor group analysis (202). Thus it seems clear that the far infra-red spectrum is sensitive to partial order, although it is not clear just how sensitive it is.

The absorption bands associated with the rotational lattice vibrations, ν_R , occur in the region 360 to 1000 cm^{-1} for ices Ih, Ic, V, and VI, and are almost featurless except for a few shoulders. Similarly, the bands due to the intramolecular vibrations in these ices are also broad and featurless. These bands are not understood in detail but presumably the factors, such as intermolecular coupling, that account for the broad absorptions in the ordered ices also contribute to the broadening of these bands. Further, the complete absence of symmetry selection rules for the rotational and intramolecular vibrations allows all vibrations to be infra-red active in the disordered phases.

The isolated OD stretching vibrations, $\nu_{OD}(\text{HDO})$, in ices Ih, Ic, V and VI occur at 2416, 2416, 2458 with a shoulder at 2495, and 2464 with a shoulder at 2500 cm^{-1} , respectively. The approximate halfwidths of these

absorptions are 20, 20, 80 and 70 cm^{-1} respectively (176, 177, 200, 203), and hence the bands are broader than the resolved bands of the ordered ices. In ice I only one crystallographic O-O bond distance exists (182), and the halfwidth of 20cm^{-1} has been interpreted (176) as arising from the small irregular variations in the O-O bond lengths which exist because the oxygen atoms are close to, but not necessarily on, the lattice sites.

Thus, it is evident that the spectra of ordered and disordered ices are considerably different. The far infra-red absorptions, caused by the translational lattice vibrations, the presence or absence of features on the ν_R band, and the breadth of the ν_{OH} (HDO) and ν_{OD} (HDO) bands in dilute isotopic samples, all indicate whether the phase is ordered or disordered.

2.3 Objectives of this Work.

(i) To seek further information on the factors effecting the absorptions by water molecules in solids formed from hydrogen bonded water.

Ethylene oxide hydrate is known to have a disordered water lattice and there is no indication that the hydrogen atoms of the water molecules are partially ordered except for short range correlations (section 1.6). The factors effecting the shapes and breadths of the absorptions in the ices, except for the ν_T absorption, are not well understood (sections 2.1 and 2.2). No successful

theoretical treatment of these absorptions has been made and hence the spectrum of the hydrate may provide more empirical information on the structural factors which influence these absorptions. The ν_T absorptions have been interpreted in terms of the density of states curves, but because these are not known for most of the ices, the influence of the crystal structure on the far infra-red spectrum is not understood in detail. Again the spectrum of the hydrate may provide further empirical information on this point.

(ii) To test the predictions of the theory of absorption by translational vibrations in orientationally disordered crystals.

The theory of absorption by translational lattice vibrations in disordered crystal predicts that factor group allowed transitions may be observed (section 2.2). So far no factor group allowed transitions have been predicted or observed in a totally disordered ice. Factor group allowed transitions are predicted for ethylene oxide hydrate and it is of interest to see if they are observed.

(iii) To determine the vibrational frequencies of the guest molecules in the hydrate.

The ethylene oxide guest molecules are known to be rotating extremely rapidly in well defined spatial regions (section 1.6), and it is of interest to compare their absorption frequencies with those of ethylene oxide

in different phases and to observe the influence of the rotation upon the absorption. No previous infra-red studies have been carried out over a wide frequency range on a characterized sample of a clathrate hydrate (section 1.6.5).

(iv) To seek evidence of different behaviour by guest molecules in different cages.

No evidence, other than X-ray data, for different behaviour by molecules in different cages has been found. In addition, calculations have shown that the local fields within different cages may vary according to the orientations of the lattice water molecules (section 1.6).

(v) To seek evidence of well defined orientations within a cage.

The X-ray studies were interpreted in terms of two preferred orientations of the guests within the tetrakaidecahedra, but no other evidence has been found to support their existence, and calculations have indicated that other orientations should be equally probable (section 1.6).

CHAPTER 3. EXPERIMENTAL TECHNIQUES.

3.1 Chemicals.

Methyl chloride, Matheson 99.5%, was condensed directly from the tank into a cold trap attached to the vacuum line. It was then distilled three times from a methanol/solid carbon dioxide bath at about -70°C before being transferred to a five litre storage flask. The infra-red spectrum of the gas was compared with a published spectrum (204) and revealed no impurities. After each sample preparation the residual methyl chloride was distilled from -70°C to remove water.

Ethylene oxide, Matheson 99.7%, was either used directly from the tank or was transferred to the vacuum line in the same way as was the methyl chloride. In the vacuum line it was triply distilled from a bath at -40°C before being stored in a five litre flask. The infra-red spectrum of the gas was compared with that observed by Potts (205) and no impurities were detected, except that water vapour was present if the sample had been rapidly distilled. Attempts were made to use anhydrous calcium chloride and other solid drying agents, but these generally adsorbed considerable amounts of the ethylene oxide. Therefore, water vapour was removed by distilling carefully from a bath at -40°C over a period of several hours.

Water, from the laboratory distilled water supply,

was either used directly or was placed in a flask on the vacuum line, carefully frozen to at least -40°C , and the air pumped off. The sample was then melted, to release any dissolved gas, refrozen and the gas again pumped off. This degassing procedure was repeated twice. 99.7% D_2O , was purchased from Columbia Organic Chemicals Company. It was found, by R. Swindlehurst using nuclear magnetic resonance techniques, to contain not more than $\frac{1}{2}$ atom % of H. It was always kept in stoppered glass bottles and handled in syringes and other glass equipment which had been pre-flushed with D_2O . Isotopic exchange with water vapour was minimized by avoiding transference through the air. The heavy water was degassed in the same way as the distilled water, but, first, D_2O was left in the vacuum line for several days to exchange with any labile hydrogen present.

3.2 Hydrate Preparation.

3.2.1 Methyl Chloride Hydrate.

Attempts were made to prepare methyl chloride hydrate by keeping about 6cm^3 of distilled water in contact with 5 litres of methyl chloride at about 650 Torr and 2°C . The reaction vessel was a large bulb attached, via a joint lubricated with silicone grease, to a tube into which the degassed water was distilled. Sufficient triply distilled methyl chloride was then condensed into the bulb to give a pressure of about 650mm of mercury at room temperature. Then, either the apparatus was placed

in a refrigerator at about 2°C, or the tube was cooled in a 'Minifreezer' to $1 \pm 0.3^\circ\text{C}$.

After a few days a crystalline layer usually formed at the water/methyl chloride interface but sometimes crystallization had to be promoted by shaking the apparatus. The solid layer was broken up by gently tapping the tube, to renew the water/gas interface. When no visible liquid remained, the excess methyl chloride was rapidly pumped off, and the tube was immediately removed and cooled in liquid nitrogen to prevent decomposition.

3.2.2 Ethylene Oxide Hydrate.

Three early ethylene oxide hydrate samples were prepared by the technique used for methyl chloride hydrate. All subsequent samples were prepared by methods 1 to 3, all based on the work of Wurtz in 1863 (46).

(1) About 5cm^3 of distilled water of the desired isotopic composition were placed in a flask, which was then fitted with an inlet tube reaching to the bottom, and an outlet tube at the top. Ethylene oxide was bubbled from a tank through the water for about 30 minutes. The flask was stoppered and placed in a cold room at $5 \pm 2^\circ\text{C}$ and left to crystallize. When crystallization was complete the crystals were removed and quickly wiped free of mother liquor, and transferred to a convenient storage vessel cooled in liquid nitrogen.

(2) About 5cm^3 of ethylene oxide were condensed from a tank into a flask, similar to the one previously described, which contained 5cm^3 of distilled water and which was cooled in an ice/salt bath. The flask, whose contents were still liquid, was then stoppered and left in the 5°C room until crystallization was complete. The crystals were then recovered and stored in liquid nitrogen.

(3) 5cm^3 of distilled water, of the desired isotopic composition, were syringed into a preweighed flask and thoroughly outgassed on a vacuum line. The closed and evacuated flask was again weighed to determine the quantity of water, and then triply distilled ethylene oxide was condensed into the flask at about 50cm of mercury pressure and 1°C . Sufficient ethylene oxide was condensed to give a 12 to 13 mole percent solution of ethylene oxide in water. After warming until any solid present had melted, the flask was again weighed to determine the amount of ethylene oxide added. The flask was kept sealed, to prevent air entering or ethylene oxide leaving, and put in the 5°C room to crystallize. Occasionally, after several weeks in the cold room without the formation of crystals, a brief cooling of the vessel was necessary to initiate crystallization, which was then completed at 5°C . The crystals were recovered and stored in liquid nitrogen.

3.3 Sample Handling, Storage and Grinding.

After the samples were prepared, they had to be handled and stored at low temperatures to avoid loss of the guest, and had to be kept in a dry atmosphere to prevent contamination by ice formed from water vapour. These requirements were met by carrying out all operations on the sample just above the surface of rapidly boiling liquid nitrogen in a large uninsulated metal can (206). Rubber gloves were always worn and the samples were handled using precooled, long-handled tweezers, spatulas and other equipment. The samples were stored under liquid nitrogen in a small, screw-capped bottle. After being closed, this bottle was placed in a larger screw-capped bottle, also containing liquid nitrogen. The cap of the larger bottle contained a split pin inserted through a hole, and a length of piano wire was fastened through this pin. After this cap was placed on the outer bottle, the whole assembly was transferred to a long necked, five litre storage dewar, and hung from the lip so that it remained under the surface of the liquid nitrogen until needed. Using these techniques, the samples were bottled in the sample handling can immediately after preparation and grinding.

A finely ground powder was necessary to ensure that sharp, clear X-ray powder patterns were obtained, and so that smooth, homogeneous mulls, which gave undistorted

infra-red spectra, could be formed. All of the methyl chloride hydrate and two of the early ethylene oxide hydrate samples were ground by hand. For this purpose, a long-handled pestle and a mortar were placed on a small table, whose top was just above the surface of the liquid nitrogen in the sample handling can. A small quantity of liquid nitrogen was poured into the mortar. The mortar, pestle and table were made of stainless steel because of its low heat conductivity. This grinding technique was tedious and sometimes it was difficult to obtain sufficiently finely ground powders. Subsequent ethylene oxide samples were placed in a grinding tube containing an impactor immediately after preparation in the cold room, and were closed before cooling in liquid nitrogen. The tube was transferred to the Spex 'Freezer Mill' grinder which contained liquid nitrogen, and the samples were ground for five periods of one minute each at maximum speed. Five minutes were allowed between each grinding to permit the heat generated during the grinding to dissipate, since the sample in this apparatus is not in direct contact with liquid nitrogen. When the grinding was completed the tube was allowed to cool for five minutes and was then removed from the liquid nitrogen, grasped using asbestos gloves, and hurriedly pried open. The open tube was immediately placed in the dry nitrogen atmosphere of the sample handling can and then the sample

was bottled.

3.4 Powder X-ray Studies.

Specimens for X-ray analysis were prepared by transferring the powdered sample with a spatula to a cold quartz capillary tube, mounted on the table of the sample handling can. The sample in the tube was packed down by gently tapping the mounting. The tube was transferred in a cold nitrogen atmosphere, created by fast boiling liquid nitrogen in a small metal pot, to a cold gas stream passing across the sample area of a Jarrel-Ash precession camera. Then the tube was mounted onto the goniometer head via a bakelite attachment fitted with a retaining grub screw which holds the sample tube in position. The cold gas stream was generated by boiling liquid nitrogen in a Dewar, using a pencil heater, and transferring the cold gas through two glass Dewar tubes to the sample area. Condensation of ice onto the sample was minimized by passing warm dry nitrogen through an outer tube coaxial with the Dewar tube (207, 208).

The sample temperature was monitored by an iron/constantan thermocouple held near the sample, and the gas flows were adjusted to give a temperature between 100 and 150°K, controlled to better than $\pm 10^\circ\text{K}$. The camera was used as a flat plate powder camera with a crystal to film distance of 6.0cm. The X-rays were generated by an

Enraf-Nonius 'Diffractis 601' generator using copper, molybdenum or chromium tubes and the appropriate nickel, zirconium or vanadium pentoxide filters to produce the $K\alpha$ radiation. Photographs were taken of the various samples of ethylene oxide hydrate and deuterate, of ice Ih and of solid ethylene oxide. Unfortunately the equipment was not available when the methyl chloride hydrate was prepared.

3.5 Infra-red Cells and Mull Preparation.

The glass infra-red gas cells had a path length of 10cm and were fitted with cesium iodide, sodium chloride or potassium bromide windows attached by 'Glyptal' or 'Araldite' cements. Liquid spectra were taken either in a conventional liquid cell fitted with cesium iodide windows separated by a teflon spacer of the required thickness, or in a low temperature condensation cell. In this cell the gas was condensed to form a liquid film between two cesium iodide windows separated by a mylar or brass spacer, 2 or 10 thousandths of an inch thick. The cell was made vacuum tight by indium gaskets held in place by suitable copper rings, a spring and a metal plate. Solid films were made by freezing the liquid in either cell and then annealing the film. Mulls were studied in cryostats which could be assembled at low temperatures.

These low temperature infra-red mull cells were made in the department's workshops and consisted of two parts,

A and B, as shown in Figure 4. The inner part, A, was a large liquid nitrogen reservoir from which was suspended a copper block, C, into which the two windows, D, containing the mull were placed. To keep the windows and mull in position in the block, a spring, E, was held and compressed by a copper plate, F, attached to the copper block by two long Allen-headed screws. The flange located on the outside of the inner part, A, fitted over two O-rings held in grooves on the top of the outer part, B, to make a vacuum tight seal. The entire cell, except the copper block, C, spring, E, and plate, F, and windows, was made from stainless steel with welded joints. The outer jacket, B, contained two windows, G, held in position against O-rings by two annular plates, H, which were fastened to the outer part, B, by two screws. The cell geometry was such that light passed directly through both outer and inner windows, with the minimum of attenuation. The entire cell was evacuated through a tap, I, at the top of the inner section, to a pressure of about 10^{-3} mm of mercury. The temperature of the copper block was monitored by a copper/constantan thermocouple, J, soldered to it, and hence an approximate value of the sample temperature was obtained. This metal cell was used for the majority of the work, but a cell of essentially the same design but made of glass (206), with a glass-metal seal for the junction to the copper block, was used for the early work. This glass

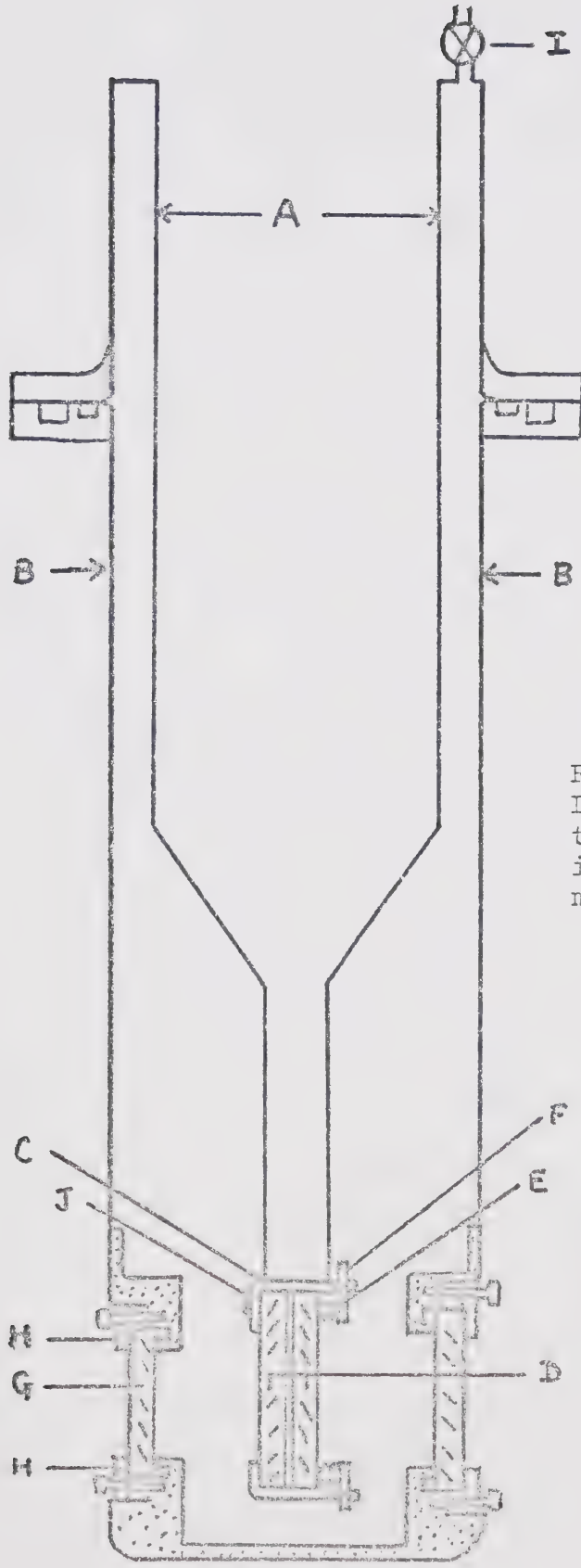


FIGURE 4.
Low
temperature
infra-red
mull cell.

cell was found to be too fragile for convenience.

For mid-infra-red spectroscopy $\frac{1}{4}$ inch thick cesium iodide discs were used as windows. They were highly polished by grinding them with aluminium oxide, then barnesite, and finally by rubbing them on a plain chamois leather, in all cases using 98% ethanol as a lubricant. For far infra-red studies $1/16$ inch thick, high density polyethylene discs were used. They were either roughened with emery paper, or cut so that the central, light transmitting area was conically tapered, thereby minimizing the interference effects within the window. When polyethylene windows were used to contain the mull, a $\frac{1}{4}$ inch thick copper disc, with a rectangular central aperture, was placed between the windows and the spring, E.

A Janis model 8DT variable temperature Dewar was used for some far infra-red work. In this cell the sample compartment is sealed against the insulating vacuum, and the sample is cooled by boiling the coolant just below it. The sample is surrounded by the cold gas and thus the sample temperature can be known more confidently and can be controlled more accurately than is the case when the sample is held in vacuum. Three sets of windows were necessary in this cell. The inner windows which contained the sample were made of tapered polyethylene, the middle windows were made of wedged crystal quartz and were sealed against indium O-rings to separate the sample compartment

from the vacuum chamber, and the outer windows were made of polyethylene.

The preparation of the mull and the assembly of the cell were carried out at about 100°K in the sample handling can (206). The most convenient can had a side arm section for use during assembly, a modification suggested and devised by M. Solinas. The two windows of the requisite material were placed, one on a stainless steel stand and the other on the table, inside the can. The inner section of the cell was suspended vertically with the copper block just touching the table, and the flange was warmed by attaching a heating tape. If polyethylene windows were being used they were cooled down, held in the copper block by the spacer, spring and plate. The can was then filled with liquid nitrogen to just below the copper block and the table top, and everything was allowed to cool.

All subsequent operations were done wearing rubber gloves and using long tweezers and long spatulas. If necessary the cell was disassembled. The sample bottle was transferred from the storage Dewar to a holder on the table. A small glass vessel was placed on the table and the mulling agent, propane, propylene or Freon 13, was condensed into it. The sample bottle was opened, a small amount of powdered sample placed on the window and a few drops of mulling agent added. The solid and liquid

were gently mixed with the tip of a spatula and then the second window was placed on top. A smooth mull was formed by rubbing the upper window gently over the lower, using tweezers placed in a slight depression in the upper window. The windows plus mull were then transferred to the cold copper block, the spring was inserted, and the outer plate was screwed into position using a long-handled screwdriver placed through a hole in the side of the can. A small amount of liquid nitrogen was placed in the coolant reservoir. The outer section of the cell, which had been flushed with dry nitrogen gas, was placed into the side arm of the can. Without removing the inner section from the nitrogen atmosphere, it was rapidly inserted into the outer section and the cell was evacuated. The warm flange enabled a rapid vacuum seal to be made. The cell was quickly transferred to the bench, filled with liquid nitrogen, and the inner and outer sections were rotated until they were aligned. The cell was then ready to be transferred to the spectrometer. While it was in the spectrometer the vacuum was maintained by continuous pumping.

3.6 Instrumentation.

3.6.1 Mid-Infra-red Region.

A Beckman IR 12 double-beam, grating spectrophotometer equipped with a fiducial marker was used to record the mid-infra-red spectra between 4000 and 200cm^{-1} . When the

sample was contained in a cryostat the lid of the sample compartment was replaced by a plexiglass cover which fitted around the cell and allowed it to be aligned in the beam while maintaining the purge. The instrument was continuously purged with either dry air to remove water vapour, or with dry nitrogen to remove both water vapour and carbon dioxide. The dry nitrogen was prepared by boiling liquid nitrogen, and passing it through a copper coil to allow it to warm to room temperature before it entered the instrument.

The fiducial marker facility was set to mark every 25cm^{-1} below 2000cm^{-1} and every 50cm^{-1} above 2000cm^{-1} . The frequencies at which the marks occurred were calibrated using the standard gases: water vapour, ammonia, carbon dioxide and hydrogen chloride (209). It was found that the calibration was readily reproduceable to better than $\pm 0.5\text{cm}^{-1}$ below 2000cm^{-1} and $\pm 1\text{cm}^{-1}$ above 2000cm^{-1} .

Routine spectra were run using twice the Standard Slit Programme of the Beckman instrument. This procedure gave a resolution of about 5cm^{-1} between 200 and 300cm^{-1} , better than 4cm^{-1} between 300 and 650cm^{-1} and about 1.5cm^{-1} between 650 and 4000cm^{-1} . Detailed studies were carried out on some of the bands at 0.5cm^{-1} resolution. The light intensity can either be recorded as the percent transmission of the cell or as the absorbance of the cell. The percent transmission scale was found to be the more

generally useful, particularly because the Variable Scale⁸⁰. Expansion facility can be used to expand the spectra of highly absorbing samples. This facility was used for most of the spectra recorded.

3.6.2 Far Infra-red Region.

Infra-red spectra in the range 360 to 17cm^{-1} were measured using a Beckman-RIIC FS 720 interferometer with non-standard electronics. The output from the Golay detector was amplified, rectified and fed to a Hewlett-Packard model 2401C digital voltmeter. The trigger signal from the mirror drive was fed to a selector, which allowed every n^{th} pulse to be used to start the digital voltmeter counting for the preset period of time. The voltage was then punched onto cards using an IBM 026 card punch driven by the voltmeter via a Hewlett-Packard model 2540B coupler.

Two driving mechanisms for the moving mirror were used, the continuous Moiré drive and the step-drive. The Moiré drive was useable over the entire frequency range, but the step-drive was found to be useable only below 250cm^{-1} , since it gave incorrect and unreproducible frequencies above 250cm^{-1} . The step-drive was somewhat superior to the Moiré drive at frequencies below about 50cm^{-1} since it was faster and gave a slightly less noisy spectrum. A variety of beam splitters and of high frequency cut-off filters purchased from Beckman Instruments Inc. were used to cover the frequency range.

The interferograms were run from $+x$ to $-x$ cm path difference. The digitized interferograms were Fourier-transformed on the IBM model 360/67 computer at the University of Alberta using BOBS IV, a Fortran IV programme written by Bertie, Othen, Brooks and Sunder, which utilizes the subroutine RHARM in the IBM scientific subroutine package. The intensity was obtained from the square root of the sum of the squares of the sine and cosine transforms. The resultant spectra were plotted on an off-line Calcomp plotter. The programme permits the ratioing of two spectra to eliminate the effects of the background and hence obtain the absorbance of the samples. It also allows the averaging of several absorbance versus wavenumber spectra to enhance the signal to noise level.

Because of the larger number of points required for a spectrum at 1cm^{-1} resolution compared to one at 3cm^{-1} resolution, the higher resolution spectra showed larger noise levels. All interferograms were run over a path difference range of at least $\pm 0.7\text{cm}$, which gave, without apodization, spectra of at least 1.5cm^{-1} resolution. However, by transforming only enough points to give a resolution of 3.5cm^{-1} the noise level was reduced to a tolerable level, without altering the spectrum significantly. When several spectra were averaged, a good spectrum was obtained using all of the data points. All interferograms were transformed using a triangular

apodization function, which decreases the noise level but also reduces the resolution by a factor of 1.5.

The calibration of the interferometer, which depends on the accuracy with which the position of the moving mirror is known, was checked several times using water vapour(210), hydrogen chloride(211), and methyl chloride (212), and was found to be within $\pm 0.2\text{cm}^{-1}$, or better, of the literature values. The only exception to this statement was in the case of the step-drive at frequencies above 250cm^{-1} , in which case the errors were very large, and the drive was not used.

3.6.3 Raman Studies.

Raman spectra were recorded on a Raman spectrophotometer which consisted of a Carson Laboratories model 10SP Ar^+/Kr^+ laser, a Spex model 1401 monochromator, a cooled I.T.T. FW130 photomultiplier, and photon counting electronics. The excitation lines at $4880\text{\AA} \text{Ar}^+$, blue, $5145\text{\AA} \text{Ar}^+$, green, $5628\text{\AA} \text{Kr}^+$, yellow, and $6471\text{\AA} \text{Kr}^+$, red, were used at a power of at least 100mW. Each sample was studied using at least two different exciting lines and reproduceable spectra with a resolution of about 1cm^{-1} and a frequency accuracy of $\pm 1\text{cm}^{-1}$ were obtained. The instrument was calibrated using benzene (213), carbon tetrachloride (214) and indene (215). The samples were liquids at about 22°C sealed in pyrex capillary tubes.

CHAPTER 4. RESULTS AND ASSIGNMENTS.

4.1 General.

The search for a definitive spectrum of a clathrate hydrate took much longer than was expected. During this investigation many factors were found to be involved in obtaining a detailed and reproduceable spectrum. Most of the early spectra had baselines which fell rapidly to high frequency so that the sample transmission at 4000cm^{-1} was 5 to 10% of that at 400cm^{-1} . Hence features at higher frequencies were not observable even with the aid of scale expansion, since scale expansion is accompanied by an increased noise level, which in these cases could not be eliminated by the use of higher time constants and slower scan speeds. Three factors were found to contribute to this poor baseline: first, inadequate grinding of the sample, second, scratched, fogged or poorly polished windows, and third, poor preparation of the mulls. All reduced the transmission at high frequencies.

A good spectrum can always be obtained if the particle size is much smaller than the wavelength of the light, which means, in this case, that particles with diameters much less than about a micron are required. This is not easily achieved and the requirement can be relaxed by suspending the particles uniformly in a liquid with a refractive index comparable to that of the particles, that is, by preparing a mull. Nevertheless, a

uniform finely ground powder is still required to form a good mull. The scattering of light by the cesium iodide windows can be reduced by very careful polishing, until a clock face can easily be read through them. 98% alcohol is required for this polishing because the water present in 95% alcohol is sufficient to fog the windows as the alcohol dries. During the mulling procedure care must be taken not to fog the outer or inner windows by bringing them into contact with moist air and one must avoid scratching the windows with any of the metal equipment or with large sample particles. Even with a finely powdered sample and well-polished windows a good spectrum need not result. If the sample is not evenly distributed throughout the mulling agent, or if the mull is not uniformly spread between the windows, then parts of the light beam are attenuated more than others. When this happens, strongly absorbing peaks in the spectrum are distorted, and in some cases the absorption maxima lose their structure and become flat topped, and the position of the baseline changes on passing through the absorption.

The mulling agents themselves also caused problems because they sometimes solidified or gave non-reproduceable peaks. Freon 13 has the highest freezing point of the three mulling agents used and was the most prone to solidification, especially when being studied alone for a reference spectrum. The spectrum of the solid Freon 13

tailed markedly to the low frequency side of the absorption, whilst on the high frequency side a small negative peak occurred followed by a sharp drop to the absorption peak. This phenomenon is due to reflection losses and is called the Christiansen Filter Effect (206). Propane was particularly prone to showing small variations in its spectrum. Some peaks would occur only in certain spectra and others would exhibit variable splittings or relative intensities. This behaviour made it extremely difficult to ascertain which features arose from sample absorption and which from mulling agent absorption. These variations could be observed in a pure sample of propane by changing the temperature slightly, and hence are probably due to phase transitions; either liquid/glass or liquid/solid transition might occur. In order to counteract the anomalous effects due to the mulling agents by keeping them in the liquid phase, a small heater was placed in the liquid nitrogen reservoir in contact with the copper block, and was controlled from a rheostat. Unfortunately, because of the thermal lag between the copper block and the sample, it was difficult to know when to stop heating, and the mulling agent often sublimed or vapourized. Freon 13 was particularly susceptible to sublimation. When this happened the hydrate sample remaining scattered light so badly that weak features above 1000cm^{-1} could not be studied. Adjusting the temperature also had the

unfortunate effect that it increased the strain in the glass-metal seals of the glass cells and they frequently broke. In order to avoid this problem, the stainless steel cell was designed, and this has proved to be very satisfactory.

Two samples of methyl chloride hydrate were prepared, ground by hand, and several mulls prepared from each sample were studied in the mid-infra-red region using glass cells. The early spectra showed steeply sloping baselines with weak, featurless absorptions at about 800 and 3200cm^{-1} due to rotational vibrations and the OH stretching vibrations of the water molecules, the $\nu_R(\text{H}_2\text{O})$ and $\nu_{\text{OH}}(\text{H}_2\text{O})$ bands, respectively. Spectra of the pure mulling agent also showed broad absorptions in these two regions and ice was clearly being incorporated into the mull during preparation. With practice the amount of ice was reduced to a tolerable level, leading to about 5% absorption in the $\nu_{\text{OH}}(\text{H}_2\text{O})$ region. Spectra of the hydrate continued to show broad featurless bands in the ν_R and $\nu_{\text{OH}}(\text{H}_2\text{O})$ regions and at 1600cm^{-1} due to the H-O-H deformation vibrations, the $\nu_2(\text{H}_2\text{O})$ band. However the bands now showed slightly steeper sides and tailed less. Both samples of methyl chloride hydrate showed identical spectra which did not improve even if the sample was ground for a prolonged time. The hydrate spectra were very similar to those of powdered ice run under similar

conditions, and showed no features that could be attributed to the guest. Further studies in all three mulling agents failed to produce substantially different spectra, and it was concluded either that the spectrum of methyl chloride hydrate under these conditions is indistinguishable from that of ice or that the sample was ice or had decomposed to form ice during grinding, storage or study. A third sample was carefully ground in an attempt to avoid decomposition but its spectra also showed no methyl chloride features and so it was decided to study a hydrate which was easily prepared and whose guest had strong infrared absorption. Ethylene oxide hydrate was chosen. In retrospect, hydrogen chloride, a common impurity in methyl chloride, may have aided the decomposition of the hydrate and, in future, the gas should be passed over potassium hydroxide pellets before preparing methyl chloride hydrate.

Three samples of ethylene oxide hydrate were prepared by the method used for methyl chloride hydrate (section 3.2). Initially the spectra appeared to be very similar to those observed previously, but for a few of the thicker mulls a very small peak was observed at about 1270cm^{-1} , where ethylene oxide is known to absorb. It thus seemed clear that ethylene oxide was present in the sample, either as a solid impurity or as a guest molecule. In order to characterize the sample a low temperature sample container was designed for the Norelco powder diffractometer. This device is not described in detail because it did not

enable satisfactory results to be obtained. It was difficult to avoid the condensation of ice in the sample, the sample could not be prepared with a sufficiently uniform surface to yield reproduceable relative intensities or even diffraction angles, and the temperature control was poor. Because of these difficulties the more intense lines of the hydrate could not be reliably distinguished from those of ice. The X-ray patterns of the ethylene oxide hydrate samples showed some features which seemed to indicate the presence of hydrate but the identification was by no means conclusive. No conclusions could be drawn about the methyl chloride hydrate samples.

X-ray photographs were also taken with the precession camera, used as a flat-plate powder camera. The methyl chloride hydrate samples were unfortunately lost and hence could not be studied further. The ethylene oxide hydrate samples were characterized with this apparatus after initial difficulties were overcome. In particular, early X-ray photographs showed hydrate patterns with superimposed ice lines but because the sample tubes became iced during transfer from the sample handling can to the camera, and during study, it was not certain if the ice was in the sample or on the outside of the tube. Subsequently, the techniques were improved so that little or no ice was deposited on the tube. Once these techniques had been developed and the samples were known to be the hydrate,

sometimes with ice Ih or ethylene oxide impurities, several samples were prepared by methods 1 and 2, ground in the Spex grinder, and used to perfect the techniques of preparing mulls and obtaining good spectra. As the techniques improved, the weak ice peaks did not appear in the background spectra, showing that ice from atmospheric water no longer contaminated the mulls, and the spectra of the hydrate showed some weak structure on the $\nu_{\text{OH}}(\text{H}_2\text{O})$ and the $\nu_{\text{R}}(\text{H}_2\text{O})$ bands. However the $\nu_{\text{OH}}(\text{H}_2\text{O})$ band resembled a poorly resolved spectrum of ice Ih, and it seemed probable that this arose from techniques that were still imperfect. The spectrum of ice Ih was therefore obtained using the same techniques, and it agreed well with the published spectra (176). Thus it was clear that the techniques had been perfected and that the $\nu_{\text{OH}}(\text{H}_2\text{O})$ band in the hydrate does indeed resemble a poorly resolved ice Ih spectrum. The spectra of the deuterate supported this conclusion, because the bands showed a considerable amount of structure, and several previously unseen absorptions due to ethylene oxide were detected. The spectra of the hydrate and the deuterate were then studied further to obtain the spectra in this thesis.

A considerable effort was made to determine the effects of small quantities of ice impurity upon the spectra. It was found that the presence of ice could be detected from the shape of the $\nu_{\text{OD}}(\text{HDO})$ absorption, due to

the O-D stretching vibration of HDO molecules in dilute solution in H_2O , with greater sensitivity than the X-ray method provided. This is discussed in detail in section 4.2.2. The spectra of samples prepared by method 3, that were shown to be free of ice by this band shape criterion, were identical with those known to contain some ice, except, of course, for the ν_{OD} (HDO) absorptions.

Attempts to obtain the far infra-red spectra of the hydrate led to a further period of difficulties, because making a mull between polyethylene windows requires different techniques from those used with cesium iodide windows. Again the reproduction of the literature spectrum of ice Ih was used as the criterion for satisfactory techniques and the spectra presented in this thesis were obtained. For the spectra below 100cm^{-1} very thick mulls are required, and to facilitate their preparation a recess was cut to a depth of 0.002 or 0.005 inches in the flat surface of one of the windows. All of the far infra-red spectra were obtained using the interferometer. Towards the end of this work it was found that the random noise could be reduced significantly by averaging three to six absorbance spectra and the computer programme was rewritten to permit this. An attempt was made to check the results from the interferometer by using the Beckman IR 11, but it was found that the beam was almost totally attenuated by the

windows and hence studies on the low temperature mulls were impossible.

The spectra of the hydrate so resemble those of ice that two hydrate samples used for far infra-red spectra were retrieved from the infra-red cell and examined by X-ray methods to ensure that the hydrate did not decompose during the infra-red experiment. The photographs confirmed that the sample was still the hydrate and no definite ice or ethylene oxide lines were seen.

From all of these studies the spectral effects of ice and ethylene oxide impurities are qualitatively known, and it is certain that the spectra presented are those of the hydrate uncomplicated by impurity absorption. The infra-red spectra of ethylene oxide hydrate at 100°K are presented in Figures 5 and 7, and those of the deuterate are presented in Figures 6 and 7. Table II contains the frequencies, approximate relative intensities, and assignments of the bands. The frequencies of the bands due to the water molecules are accurate to about $\pm 5\text{cm}^{-1}$, except as noted in Table II, because of the breadth of the bands. The frequencies of the more intense ethylene oxide features are accurate to $\pm 1\text{cm}^{-1}$, while those of the less intense features are probably only good to $\pm 2\text{cm}^{-1}$. Above 100cm^{-1} the assignment of the bands to host or guest absorption followed from the water isotope shifts. The detailed assignments are discussed in the next sections of

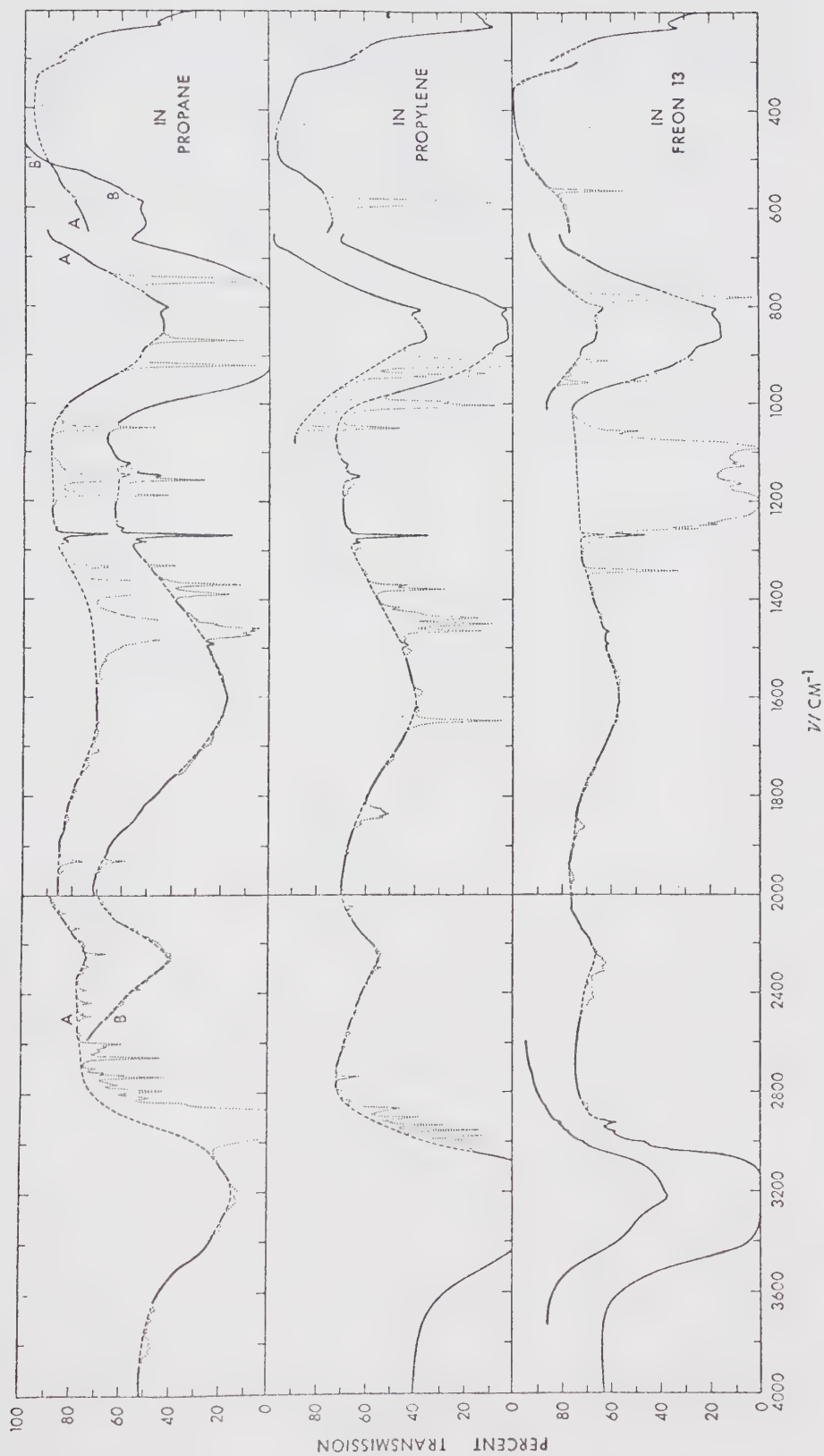


FIGURE 5. Mid-infrared spectra of mulls containing ethylene oxide hydrate at 100°K. The dotted lines indicate the absorptions due to the mulling agents while the dashed lines indicate the hydrate absorptions in these regions.

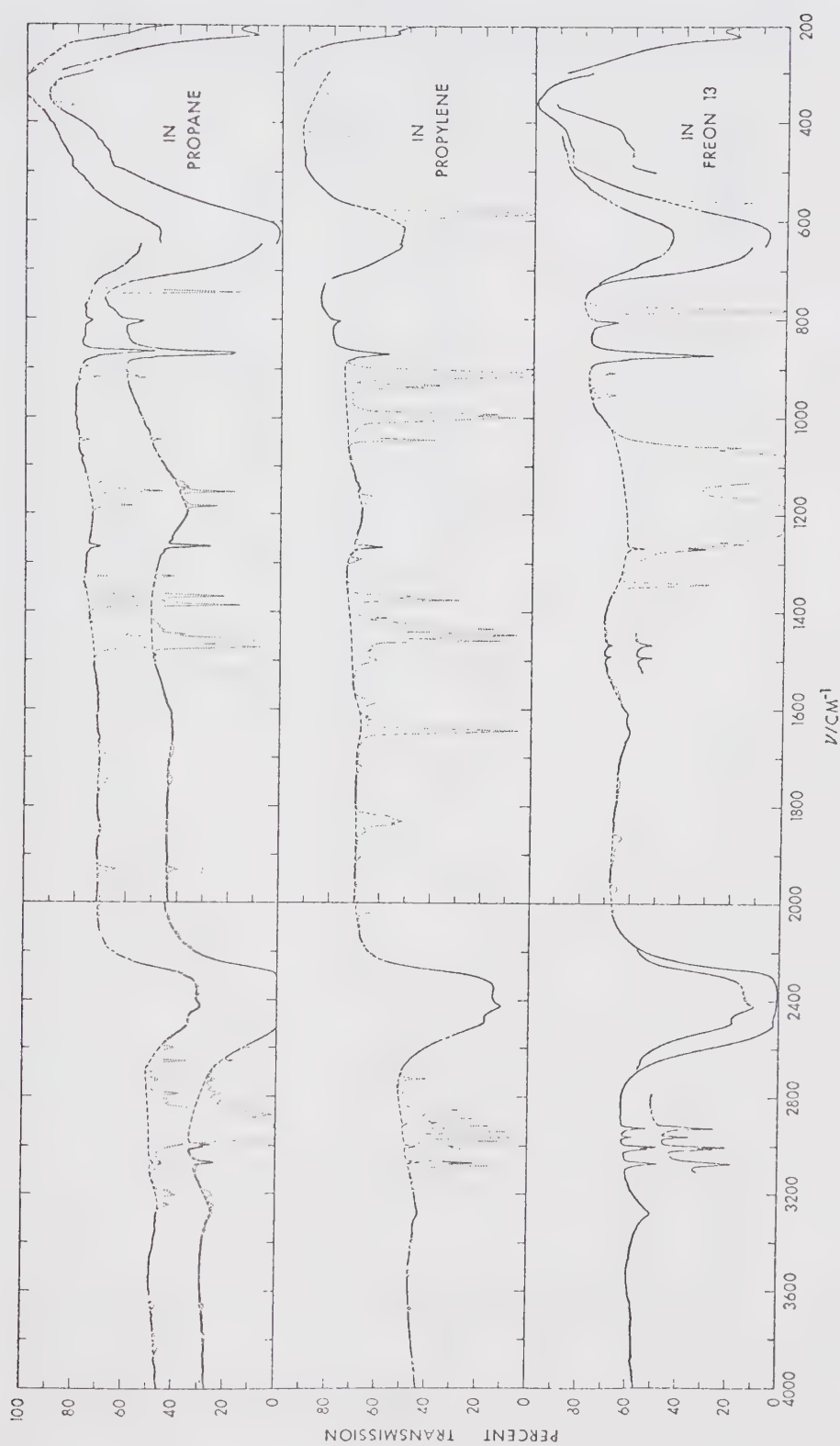


FIGURE 6. Mid-infrared spectra of mulls containing ethylene oxide deuterate at 100°K. The dotted lines indicate the absorption due to the mulling agent while the dashed lines indicate the deuterate absorptions in these regions.

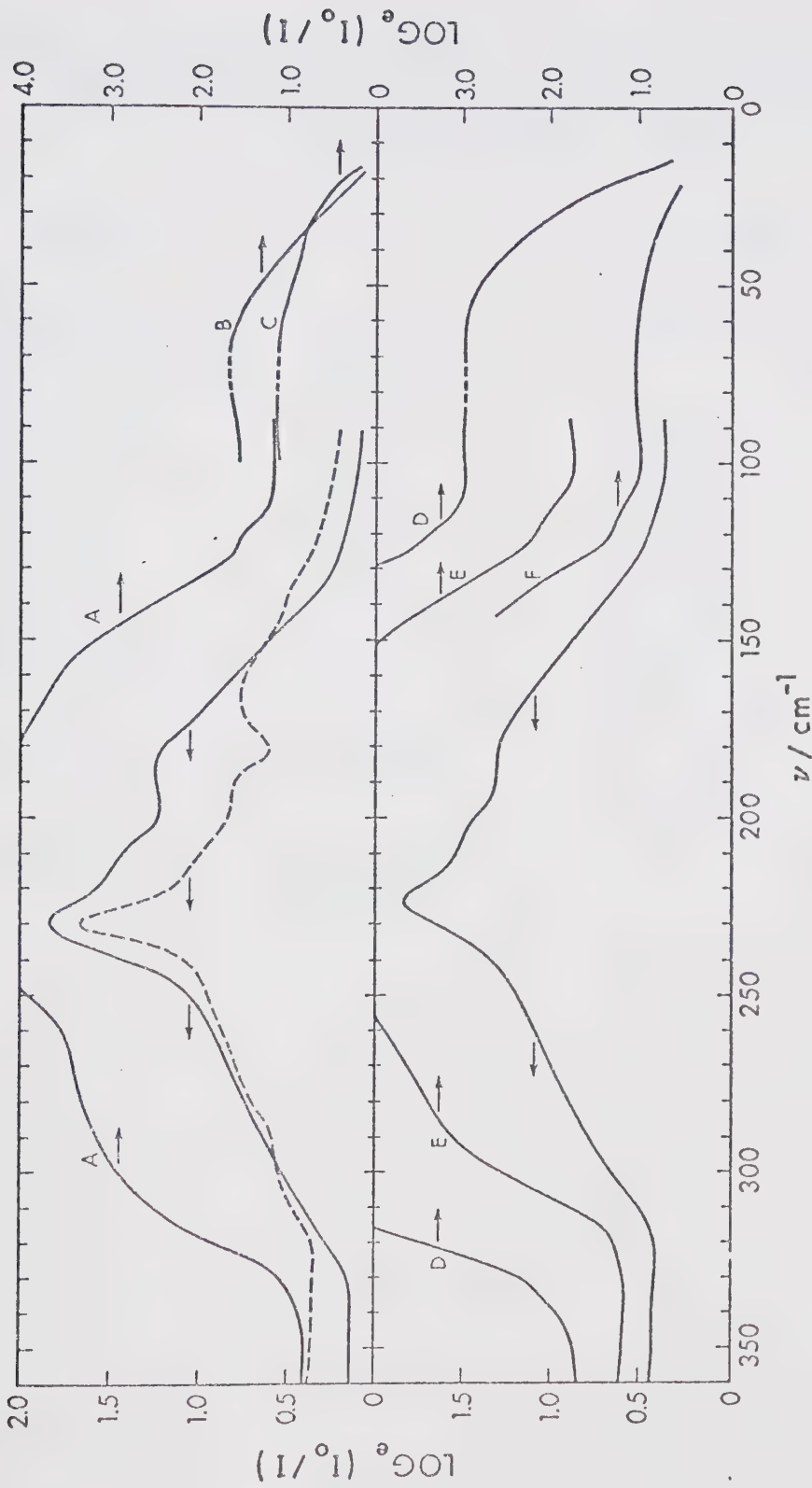


FIGURE 7. Far infra-red spectra of ethylene oxide hydrate (upper box) and ethylene oxide deuterate (lower box) at about 100°K. The dashed line is the spectrum of ice I obtained using the same techniques.

TABLE II. FREQUENCIES IN CM^{-1} OF FEATURES OBSERVED IN THE
INFRA-RED SPECTRA OF ETHYLENE OXIDE HYDRATE AND
DEUTERATE AT ABOUT 100°K.

<u>HYDRATE</u>		<u>DEUTERATE</u>	
3400 sh.	}		
3220 v.s.br.		3272 br.	$\nu_{\text{OH}}(\text{HDO})$
3100 sh.			
3066 w.		3069 m.	
3009 w.		3008 m.	
2998 w.		2999 m.	
2957 w.		2958 m.	
2920 w.		2922 m.	
2913 v.w.		2914 w.	
		2490 br.sh.	}
2424 br.	$\nu_{\text{OD}}(\text{HDO})$	2425 br.s.	
		2333 br.sh.	
2250±15 v.br.w.	{		
	$\nu_2 + \nu_R,$	1630±15 m.br.	{
	$3\nu_R(\text{H}_2\text{O})$	1610 sh.	
1605±20 v.br.m.	$\nu_2(\text{H}_2\text{O})$		
1489 w.	E.O.	1491 w.	
1466 w.	E.O.	1467 w.	
1282 w.	E.O.	1282 w.	
1270 m.	E.O.	1270 m.	
1268 v.s.	E.O.	1268 v.s.	
1255 v.w.	E.O.	1255 v.w.	
		1200±15w.br.	$\nu_2(\text{D}_2\text{O})$
1147 w.	E.O.	1147 w.	
1123 v.w.	E.O.	1122 v.w.	
890 sh.	$\nu_R(\text{H}_2\text{O}) + \text{E.O.}$	881 sh.	E.O.
864 i.	$\nu_R(\text{H}_2\text{O}) + \text{E.O.}$	872 v.s.	E.O.
845 s.br.	$\nu_R(\text{H}_2\text{O})$		

TABLE II. Continued.

<u>HYDRATE</u>		<u>DEUTERATE</u>
808 sh.	E.O.	810 sh.
805 s.	E.O.	807 s.
630 w.sh.	$\nu_R(\text{H}_2\text{O})$	680 sh.
590 w.sh.?		620 s.br.
560 w.sh.		465 w.sh.
530 w.sh.		422 w.sh.
~335 i.	$\nu_T(\text{H}_2\text{O})$	~320 i.
~300 sh.		~290 sh.
250 i.		240 i.
229.6±0.9 s.		223.1±0.5 s.
210 sh.		203 sh.
198 min.		180 sh.
184 w.		114 sh.
120 sh.		105 i.
110 i.		
50 - 60	low frequency edge of plateau.	45 - 55

E.O. indicates that the feature is assigned to an ethylene oxide guest vibration. The explanation of the abbreviations is: v.= very; s.= strong; m.= medium; w.= weak; br.= broad; sh.= shoulder; i.= point of inflection; min.= minimum.

All features below 360cm^{-1} were studied using the interferometer; above this frequency the Beckman IR 12 was used.

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this chapter along with more detailed comments on the individual bands.

It remains here only to justify the claim that the sample temperature was 100°K because it is well known that the temperatures of samples held in vacuum are difficult to measure reliably. For the mid-infra-red region the Freon 13 mulling agent often froze, indicating a sample temperature of close to 95°K . To allow for uncertainties in the temperature reached upon heating, $100 \pm 10^{\circ}\text{K}$ is cited as the sample temperature when cesium iodide windows were used. Polyethylene windows, however, have a lower thermal conductivity than cesium iodide windows and hence the far infra-red mulls may have been at higher temperatures. In an attempt to measure this temperature, a thermocouple was embedded in a polyethylene window, but it showed a very slow response, probably because of the difficulty of creating good thermal contact in a vacuum, and the lowest temperature recorded was 125°K . However, when the windows were separated after spectra had been recorded, liquid propane or propylene was still present. It seems unlikely that these mulling agents would remain in a vacuum for at least 10 hours at 125°K and hence the temperature was probably about 100°K but it is impossible to be certain of the exact temperature. The temperature of the copper block was monitored at between 80 and 95°K .

Because of this uncertainty in the temperature,

which was considered to be particularly serious for the study of the ethylene oxide intermolecular vibrations below 100cm^{-1} , spectra in this region were also recorded in the Janis model 8DT cell. The sample temperature in this cell was controlled at $90 \pm 1^\circ\text{K}$. The spectra were identical with those obtained using the other cell.

4.2 Absorption due to the Host.

4.2.1 H_2O and D_2O Absorptions.

A comparison of the spectra of the hydrate and deuterate with that of ice I (176) immediately yields the assignment of the bands due to the vibrations of the host water molecules in the hydrate. Thus the absorptions near 3220, 2270, 1600, 840 and below 360cm^{-1} in the hydrate can be assigned to the $\nu_{\text{OH}}(\text{H}_2\text{O})$, $3\nu_{\text{R}}$ and $\nu_2 + \nu_{\text{R}}$, $\nu_2(\text{H}_2\text{O})$, $\nu_{\text{R}}(\text{H}_2\text{O})$ and $\nu_{\text{T}}(\text{H}_2\text{O})$ vibrations, respectively. In the deuterate the absorptions near 2420, 1630, 1200, 620 and below 360cm^{-1} are assigned to $\nu_{\text{OD}}(\text{D}_2\text{O})$, $3\nu_{\text{R}}$ and $\nu_2 + \nu_{\text{R}}$, $\nu_2(\text{D}_2\text{O})$, $\nu_{\text{R}}(\text{D}_2\text{O})$ and $\nu_{\text{T}}(\text{D}_2\text{O})$, respectively. The definition of the symbols is given in chapter 2.

The extremely strong $\nu_{\text{OH}}(\text{H}_2\text{O})$ absorption in the hydrate has a central peak at 3220cm^{-1} and shoulders at 3100 and 3400cm^{-1} . It is very similar to that of ice Ih (176) which has features at 3220, 3150 and 3380cm^{-1} respectively. The frequency differences are probably not significant because the features are poorly defined. Both bands are broad, with halfwidths of about 400cm^{-1} , but the

hydrate features are less well defined. The strong $\nu_{OD}(D_2O)$ absorption in the deuterate has a peak at 2425cm^{-1} and shoulders at 2333 and 2490cm^{-1} compared with values of 2425 , 2332 and 2485cm^{-1} respectively in D_2O ice (176). The bands in the deuterate and D_2O ice both have halfwidths of about 250cm^{-1} although in D_2O ice the features are more pronounced and there are two weak shoulders at 2395 and 2545cm^{-1} (176). In both phases, the features on the 2420cm^{-1} band are more clearly resolved than those on the 3220cm^{-1} band.

The overtone, $3\nu_R$, and combination, $\nu_2 + \nu_R$, overlap to form a weak broad band centred at 2270cm^{-1} in the hydrate and at 2266cm^{-1} with a shoulder at 2450cm^{-1} in ice I (176, 216). For the deuterate this absorption occurs at about 1630cm^{-1} with a shoulder at about 1610cm^{-1} , whilst in D_2O ice the band is centred at about $1650 \pm \sim 30\text{cm}^{-1}$ (176). A further broad weak absorption due to the ν_2 vibration and the $2\nu_R$ overtone occurs at about 1605cm^{-1} in the hydrate and about 1200cm^{-1} in the deuterate. For H_2O and D_2O ice I the reported frequencies are 1600 (216) and 1210cm^{-1} (176) respectively. All the ν_2 and $2\nu_R$ bands are extremely broad, weak and almost featurless.

The ν_R band in the hydrate is centred at 840cm^{-1} as is the same absorption in ice I. The hydrate and ice bands are both broad and have halfwidths of about 160cm^{-1} . However, the hydrate band shows features not observed in

ice I. The peak at 805cm^{-1} with a weak shoulder at 808cm^{-1} ^{100.} is clearly due to ethylene oxide absorption and is observed in the deuterate at 807 and 810cm^{-1} respectively. However, the sharp change in absorption at 864cm^{-1} leading to a weak shoulder at 890cm^{-1} does not correlate so well with the ethylene oxide absorption at 872cm^{-1} and shoulder at 881cm^{-1} seen in the deuterate. No features corresponding to the shoulders at 770 and 900cm^{-1} in ice I are observed in the hydrate, but a feature is observed at 560cm^{-1} which is rather more pronounced than the 555cm^{-1} shoulder in ice I. There are also weak features in the hydrate at 630 , 530 , and possibly 590cm^{-1} which do not occur in ice I. The $\nu_R(\text{D}_2\text{O})$ bands in the deuterate and D_2O ice both have halfwidths of about 120cm^{-1} . The deuterate band peaks at 620cm^{-1} while that in ice I is reported at 640cm^{-1} , although from curve a of Figure 3 of reference 176 it appears to peak at 625 to 630cm^{-1} . In both phases the strong absorption is asymmetric with a change of slope at about 675cm^{-1} .

Below 360cm^{-1} absorption by the translational lattice vibrations, ν_T , is observed. The spectra of the hydrate and deuterate down to 100cm^{-1} are similar. They consist of a broad peak, at 229.6 and 223.1cm^{-1} respectively together with one high frequency shoulder, two low frequency shoulders and a peak to low frequency of the central maximum. In ice and D_2O ice (198) broad spectra

are observed with peaks at 229.2 and 221.7cm^{-1} , respectively, which are sharper than the peaks of the hydrate and deuterate. The most noticeable difference between the far infra-red spectra of the hydrate and ice, and the deuterate and D_2O ice, is the absence of a dip near 180cm^{-1} in the clathrates.

Below 100cm^{-1} the absorption in ice I steadily decreases with decreasing frequency (198) with a weak shoulder at about 65cm^{-1} (216). Experimental and theoretical studies have shown that from 45 to 25cm^{-1} the absorptivity at 100°K is proportional to ν^4 whilst down to 17cm^{-1} , it is proportional to ν^2 (199). All other phases of ice studied (173) also show approximately linear decreases in absorption below 100cm^{-1} down to the lowest frequencies studied except ice V, which shows a small peak at 95cm^{-1} . In contrast the clathrates show a broad plateau between 100 and about 50cm^{-1} with an essentially linear decrease in absorption below this frequency. Because of the low frequency and breadth of the absorption and the extreme difficulty of determining its exact shape no isotope shift has been detected. It seems likely that at least part of this hydrate absorption is not associated with water lattice vibrations. The assignment will be discussed in detail in a later section.

4.2.2 HDO Absorptions.

In dilute isotopic samples, absorptions due to the

stretching vibrations of the OH and OD bands of HDO are observed, $\nu_{\text{OH}}(\text{HDO})$ and $\nu_{\text{OD}}(\text{HDO})$, respectively. $\nu_{\text{OD}}(\text{HDO})$ was studied in samples made by methods 1, 2 and 3 from solutions containing 1 to 5% of D_2O in H_2O . In practice a 1% D_2O in H_2O sample contains about 0.01% of D_2O molecules and almost 2% of HDO molecules but samples are designated in terms of the percentage concentrations of D_2O placed in the preparation flask. The spectra of these samples were identical to that of the corresponding hydrate or deuterate together with the $\nu_{\text{OD}}(\text{HDO})$ or $\nu_{\text{OH}}(\text{HDO})$ absorption respectively.

Studies were first carried out on two samples made by method 1 containing 1 and 5% of D_2O respectively. Both samples showed $\nu_{\text{OD}}(\text{HDO})$ peaks which were steep and straight sided and sharp pointed, as shown in curve a of Figure 8. These peaks are referred to as V-shaped peaks. Both samples showed peak maxima at 2419cm^{-1} but the 5% sample gave a broader band of about 65cm^{-1} halfwidth, whilst the $\nu_{\text{OD}}(\text{HDO})$ band in the 1% sample had a halfwidth of about 40cm^{-1} . The X-ray patterns of both samples showed ice lines.

Subsequently two samples were made from 2% and 5% D_2O in H_2O respectively by method 2. The 2% sample showed weak peaks at the frequencies where strong absorption occurs in solid ethylene oxide. Figure 9 shows the absorption between 750 and 950cm^{-1} for a sample which is

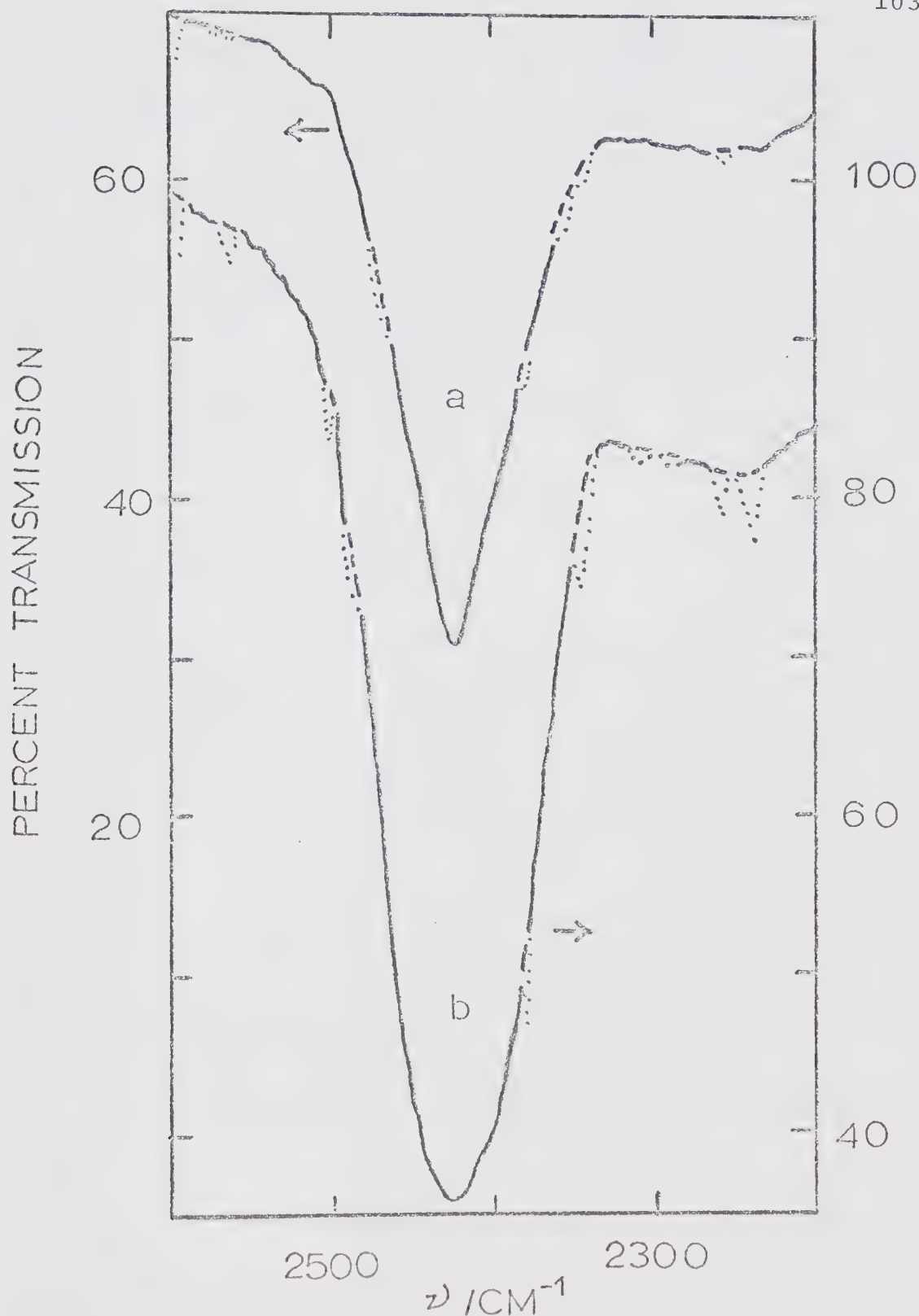


FIGURE 8. Absorption by $\nu_{\text{OD}}(\text{HDO})$ in 5% D_2O ethylene oxide hydrate at 100°K . Curve a is from a sample contaminated with ice I while curve b is from a pure sample.

impurity free, curve a, and for the 2% sample which contains excess solid ethylene oxide, curve b. For comparison, Figure 10 shows the spectrum of solid ethylene oxide in the same region, and the arrows in Figure 9 indicate the absorptions associated with the solid ethylene oxide. The powder X-ray pattern of this 2% sample gave no indication of ice, but exhibited weak features in the regions where ethylene oxide lines occur. These features could not be positively identified because they merged into the background. Hence this sample is probably ice free but contains a small amount of ethylene oxide. It was not possible to observe any features attributable to solid ethylene oxide in the infra-red spectrum of the 5% sample but its X-ray pattern showed no ice or ethylene oxide features. It is therefore thought to be almost impurity free. The ν_{OD} (HDO) bands for both samples were broader, not as steep and straight sided and less pointed than those previously observed, as in curve b of Figure 8, and are referred to as U-shaped. The halfwidths were about 80 and 88 cm^{-1} for the 2 and 5% samples respectively and the flat topped bands were centred at about 2428 and 2424 cm^{-1} .

A total of five samples made from 1, 2 and 5% D_2O in H_2O by method 3 were studied. These samples should be homogeneous and should not be contaminated by ice or ethylene oxide since the work of Glew and Rath (82)

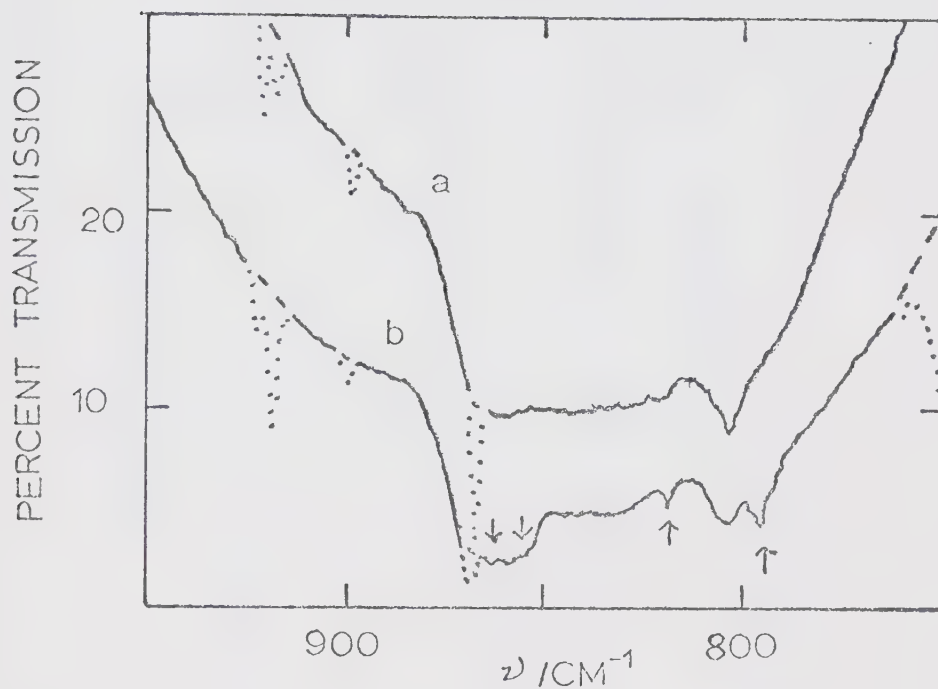


FIGURE 9. Absorption by ethylene oxide hydrate at 100°K. Curve a is from a pure sample while curve b is from a sample containing solid ethylene oxide. The arrows indicate the absorptions by the solid ethylene oxide.

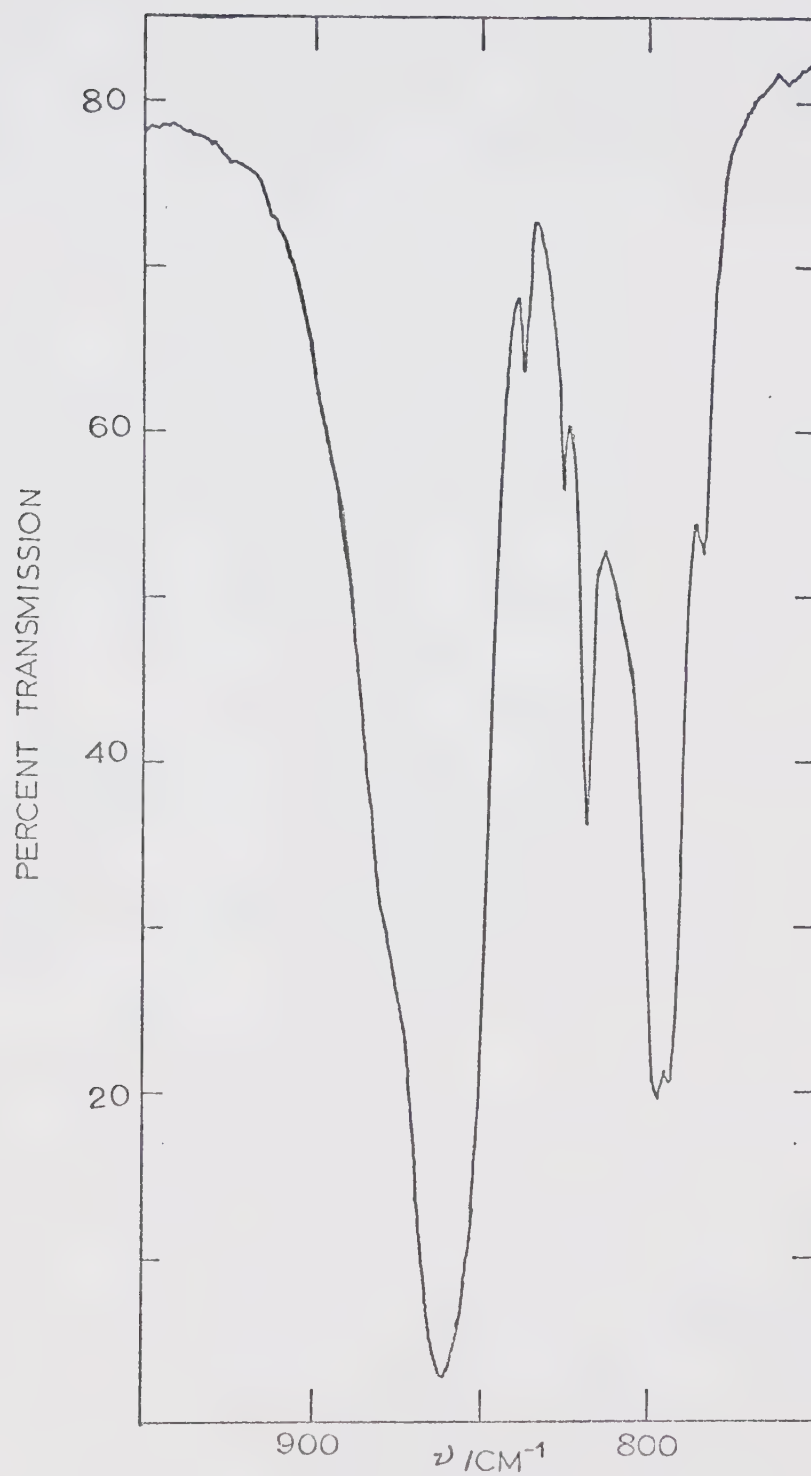


FIGURE 10. Absorption by solid ethylene oxide at 100°K.

indicates that samples grown from a 12.7 mole percent solution should have a stoichiometry of $6.8\text{C}_2\text{H}_4\text{O} \cdot 0.46\text{H}_2\text{O}$ and hence the solid and solution compositions should remain the same throughout the crystallization. All these samples had X-ray powder patterns which contained no ice lines.

ν_{OD} (HDO) peaks in these samples were not as sharp pointed as those for samples prepared by method 1, and showed a gradation in shapes from an extreme U-character to an intermediate shape between that of the U and V extremes. The halfwidths ranged from about 62 to 84cm^{-1} and the frequencies from about 2417 to 2428cm^{-1} . The weakness of the peaks in the 1 and 2% samples makes it difficult to measure the halfwidths or frequencies accurately whereas, in the 5% sample, some of the HOD molecules might be close enough to allow some intermolecular coupling with resultant broadening of the peak. Nevertheless the overall shape of the absorption was unmistakable.

Ice Ih is known to have a sharp-pointed ν_{OD} (HDO) absorption band with a halfwidth of about 18cm^{-1} at 2418cm^{-1} (203) and it was considered possible that small amounts of HDO ice in the sample affected the ν_{OD} (HDO) band. Therefore, the ratio of HOD absorbance to that of the 1268/1270 doublet was measured. Initially the results were complicated by inadequate resolution of the doublet but it was found that for the 5% samples prepared by method 1 the ratio was about 1.1 whereas for samples

prepared by method 3 it lay between 0.8 and 0.9, the lower value being associated with the broader and more U-shaped peak. A low value was also obtained for the sample prepared by method 2 but experimental difficulties and the possible presence of excess solid ethylene oxide made this result unreliable. The ν_{OD} (HDO) bands were replotted on an absorbance scale and the areas were measured but the ratios were almost the same as those obtained by using absorbances. The higher absorbance ratios found for the samples that showed V-shaped ν_{OD} (HDO) peaks argues that ice absorption does contribute to these peaks.

This explanation was finally confirmed by taking a 5% sample prepared by method 3, and keeping it at -2°C for twelve hours in a closed vessel, before recooling to -195°C . This technique should produce some decomposition of the hydrate to form ice but there should be little or no loss of ethylene oxide by the bulk of the sample since the lattice is not broken. Initially the sample gave a U-shaped ν_{OD} (HDO) peak which is shown in curve b of Figure 8. The peak has a halfwidth of about 84cm^{-1} , a frequency of about 2423cm^{-1} and an absorbance ratio for the HOD/ 1268cm^{-1} peaks of 0.8. After heating and recooling, the sample exhibited an essentially V-shaped peak which is shown in Figure 11. The peak has a halfwidth of about 79cm^{-1} , a frequency of about 2421cm^{-1} and an absorbance ratio of 1.0. The X-ray pattern of the warmed sample

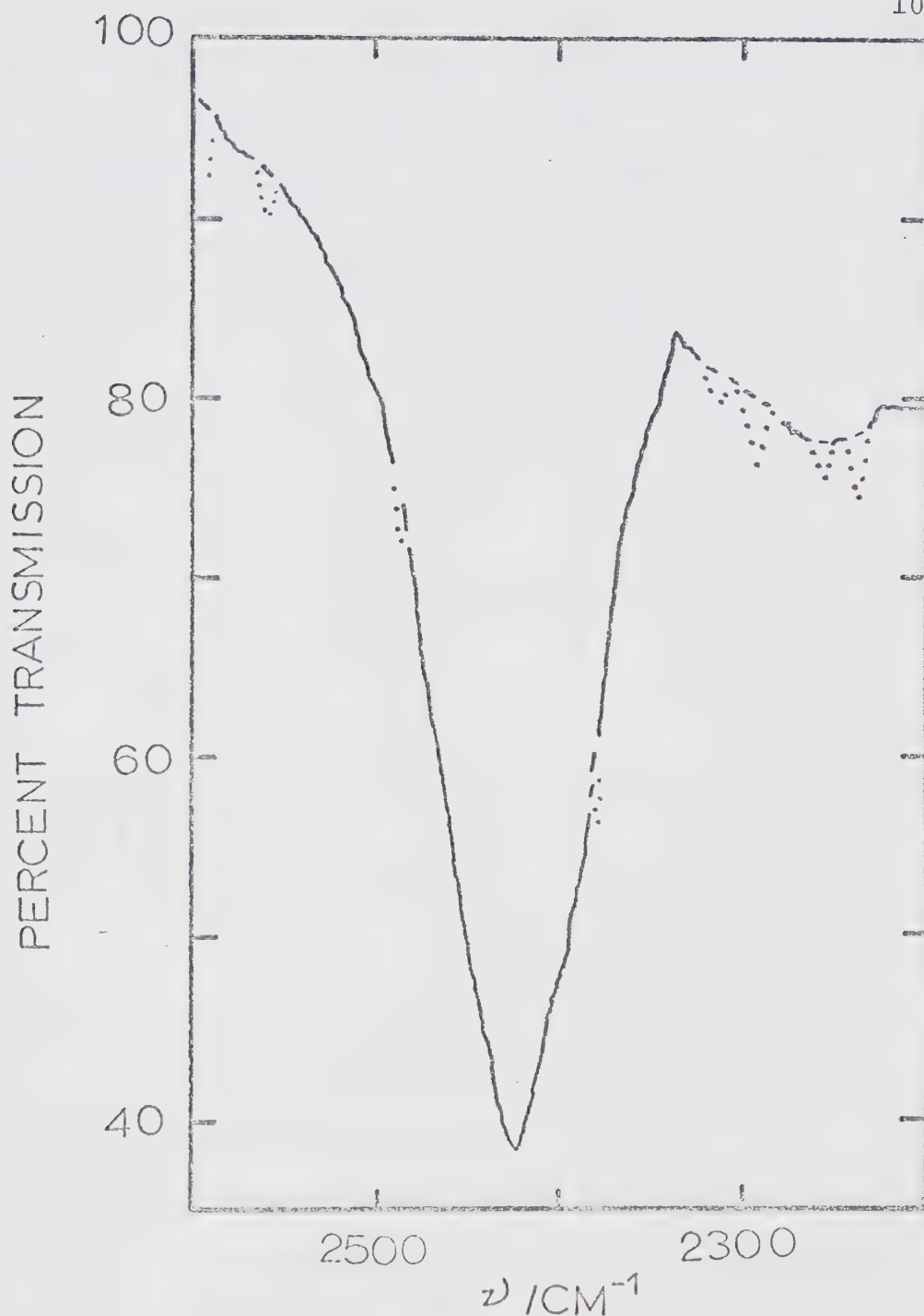


FIGURE 11. Absorption by ν_{OD} (HDO) in 5% D_2O ethylene oxide hydrate at 100°K . The sample was the same as that for curve b of Figure 8 except that it had been held at -2°C for 12 hours and recooled.

differed from that of the initial sample by showing a very weak haze in the region of the ice lines.

From all this evidence it was concluded that the presence of HDO ice in the sample causes a sharper and stronger $\nu_{\text{OD}}(\text{HDO})$ absorption and that samples prepared by methods 2 and 3 were usually ice free whereas those prepared by method 1 usually contained ice. The average of the best ice free 5% D_2O in H_2O samples prepared by methods 2 and 3 gives a halfwidth for $\nu_{\text{OD}}(\text{HDO})$ of $85 \pm 5 \text{ cm}^{-1}$ at 2424 cm^{-1} . The corresponding 2% samples have values of $78 \pm 5 \text{ cm}^{-1}$ at 2428 cm^{-1} whilst the 1% has a peak of half-width $70 \pm 10 \text{ cm}^{-1}$ at about 2428 cm^{-1} , but this sample may not be entirely ice free. The differences between samples of different D_2O content are probably not significant because of the low intensity of the peaks, the roundness of the peak and the difficulty of obtaining totally ice free samples. An overall value for the halfwidth of $\nu_{\text{OD}}(\text{HDO})$ of about $80 \pm 10 \text{ cm}^{-1}$ at a frequency of about $2427 \pm 3 \text{ cm}^{-1}$ would seem appropriate.

The $\nu_{\text{OH}}(\text{HDO})$ band was studied in samples made by methods 1 and 3 from solutions of 0.3 to 5% H_2O in D_2O , designated 99.7 to 95% D_2O samples. The band must be studied in the absence of ice Ih or vitreous ice contaminants, which can enter during mull preparation, since both cause an additional broad absorption with a halfwidth of at least 200 cm^{-1} . The samples prepared by

method 1 had pointed V-shaped ν_{OH} (HDO) bands which have halfwidths as low as 75cm^{-1} at about 3275cm^{-1} , as shown in Figure 12a. However, these were believed to contain HDO ice because of the method of preparation, the band shape, the halfwidth and the X-ray photographs. 95.5 and 97.5% samples made by method 3 were therefore studied since they were believed to be ice free. These four samples give broad featurless bands which have rounded tops, as shown in Figure 12b. Because of their shape it was difficult to ascertain either the halfwidth or the peak frequency accurately but the average values are about $125 \pm 15\text{cm}^{-1}$ at about $3272 \pm 10\text{cm}^{-1}$.

4.3 Absorption due to the Guest.

The absorptions due to the ethylene oxide molecules will be discussed generally in this section and the detailed assignment will be considered in the next section, section 4.4.

The ethylene oxide absorptions caused by intramolecular vibrations must be studied carefully in both the hydrate and deuterate because the strong, broad, water absorptions often obscure the weaker, sharper ethylene oxide bands. It is also essential to examine samples in all three mulling agents because some of the weaker guest features are partly covered by peaks of one or more mulling agents. A case in point is the 1123 and 1147cm^{-1} peaks, which are only observable in propane and propylene

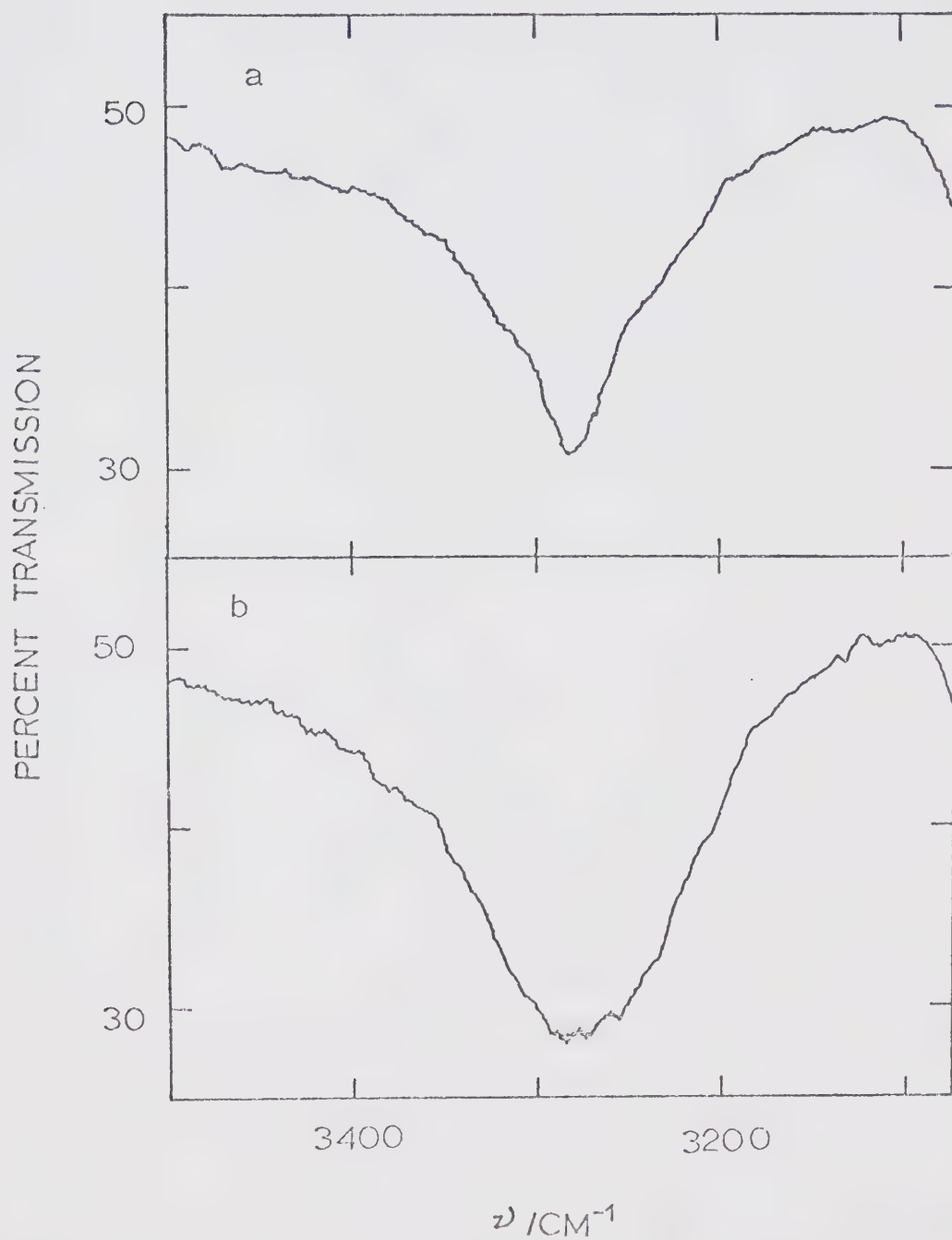


FIGURE 12. Absorption by $\nu_{\text{OH}}(\text{HDO})$ in ethylene oxide deuterate at 100°K . Curve a is from a sample contaminated with ice I while curve b is from a pure sample.

and, even in these mulling agents, the peaks are partly obscured. Further the low concentration of the guest in the clathrate, about 13%, necessitates a study of very thick mulls which often have strong background absorption. Hence extreme Variable Scale Expansion must be used and this raises the noise level thereby hindering the study further and requiring slow scan speeds and high time constants. It is not surprising, therefore, that the early studies only located the 1270cm^{-1} absorption in the hydrate. Improved mulls, more finely ground samples, and better spectra eventually led to the identification of the ethylene oxide absorption features designated by the letters E.O. in Table II. Figures 5 - 7 show the overall spectra of the hydrate and deuterate whilst more detailed spectra of the intramolecular ethylene oxide absorptions are shown in Figures 13a, 14a, 14b, 15, 16a.

The authenticity of these absorptions was carefully checked by using different mulls, different mulling agents and hydrate or deuterate samples prepared by different techniques. The final confirmation that the peaks were due to enclathrated ethylene oxide was obtained when mulls of a sample made by method 2 showed all the absorptions associated with the guest together with additional absorptions at the frequencies at which solid ethylene oxide absorbs. Curve a of Figure 9 shows the spectrum between 750 and 950cm^{-1} of a pure hydrate sample at 100°K ,

prepared by method 3, and uncontaminated by ice or ethylene oxide. The broad absorption is the $\nu_R(\text{H}_2\text{O})$ band whilst the features at 805, 808, 864 and 890cm^{-1} are associated with the enclathrated ethylene oxide. Curve b of Figure 9 shows the analogous spectrum for a sample, prepared by method 2, containing excess solid ethylene oxide and, for comparison, the spectrum of solid ethylene oxide at 100°K in the same region is shown in Figure 10. The arrows in Figure 9 indicate the additional features in the hydrate spectrum caused by the solid ethylene oxide.

The absorptions associated with the intramolecular vibrations of the guest ethylene oxide molecules are all sharp, generally with halfwidths of about 3 to 5cm^{-1} unless there is overlapping with other absorptions. In the region 2800 to 3200cm^{-1} shown in curve a of Figure 13, six peaks are observed. The frequencies in the hydrate and deuterate are almost identical, the greatest difference being 3cm^{-1} for the peak closest to the $\nu_{\text{OH}}(\text{H}_2\text{O})$ band maximum. The bands are best seen in the deuterate where the frequencies are 2914, 2922, 2958, 2999, 3008 and 3069cm^{-1} . The resolution in this region was about 1.0cm^{-1} . The 3069cm^{-1} peak is exceptionally broad with a halfwidth of almost 10cm^{-1} . The weak Freon 13 absorption in this region is indicated in Figure 13 by dotted lines. Figure 14b shows the region between 1450 and 1500cm^{-1} ,

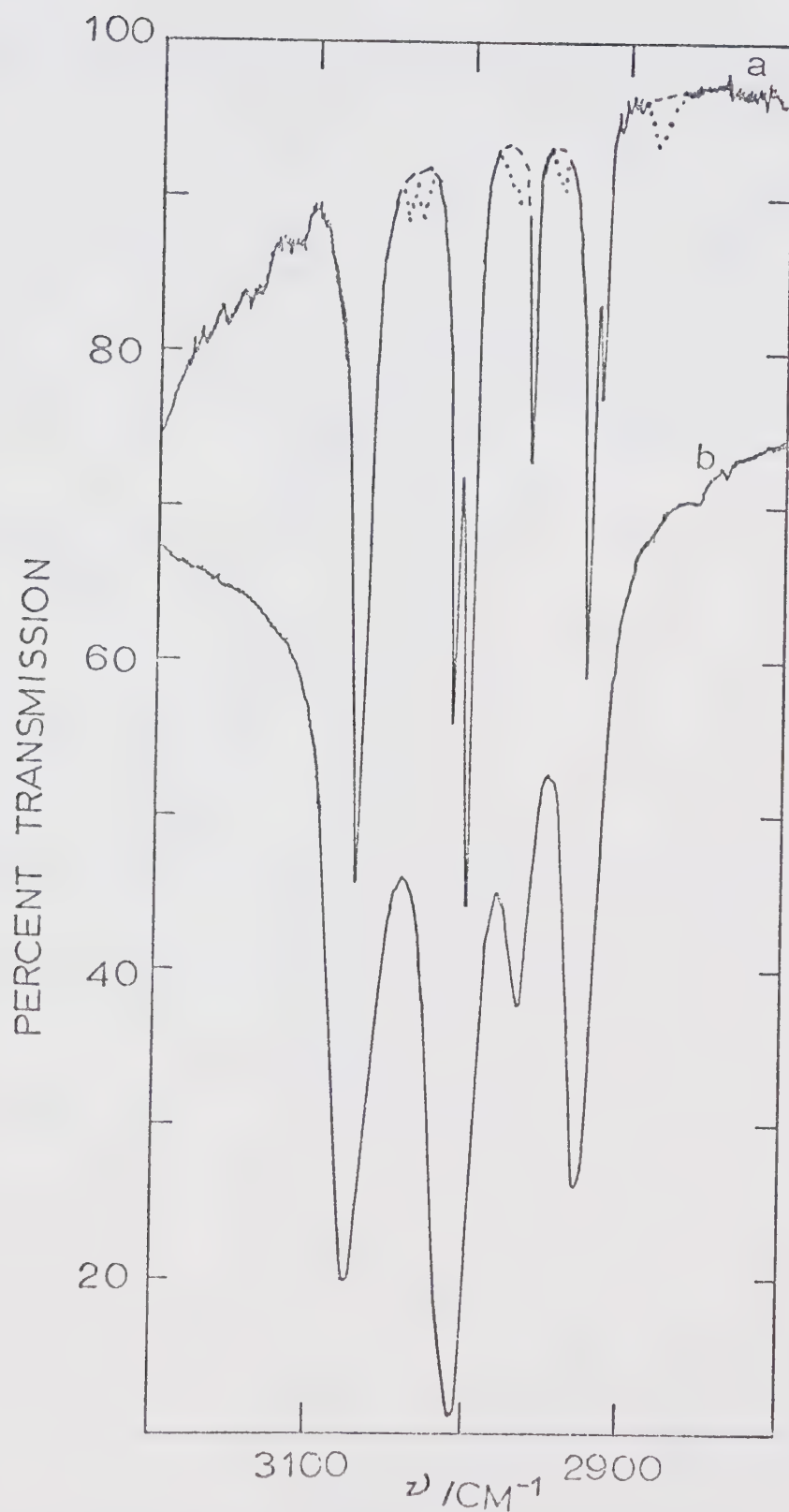


FIGURE 13. Absorption by ethylene oxide in ethylene oxide deuterate at 100°K (curve a) and in liquid ethylene oxide at 210°K (curve b).

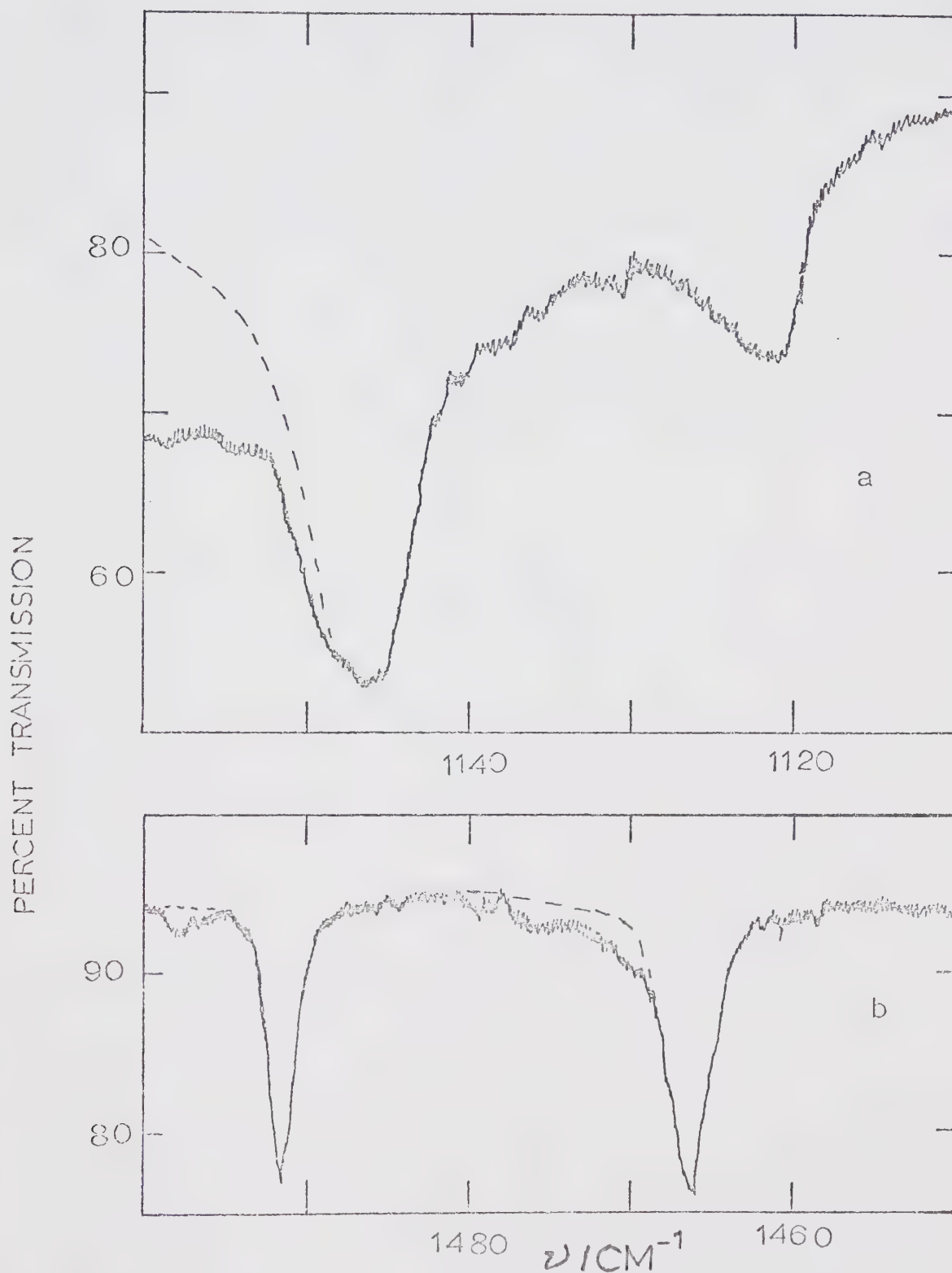


FIGURE 14. Absorption by ethylene oxide in ethylene oxide hydrate (curve a) and in ethylene oxide deuterate (curve b) at 100°K. The dashed line indicates the curve approximately corrected for absorption by the mulling agent.

where there are two peaks due to ethylene oxide absorption¹¹⁷. They occur at 1466 and 1489 cm^{-1} in the hydrate and 1467 and 1491 cm^{-1} in the deuterate, but they are so weak that they are not readily observed, and hence the difference in measured frequencies is not significant. Weak Freon 13 absorption occurs in this region and the dashed line in Figure 14b indicates the estimated deuterate absorption. It is conceivable that very weak shoulders are hidden by the mulling agent absorption. The peak halfwidths are about 2 cm^{-1} .

The strongest guest absorption in the hydrate occurs at 1268 cm^{-1} and was the first to be observed. In the deuterate, this peak is situated on the side of the $\nu_2(\text{D}_2\text{O})$ and $2\nu_{\text{R}}(\text{D}_2\text{O})$ band and, consequently, the background transmission is low and a detailed quantitative study is very difficult. However, the two peaks are qualitatively identical. Under routine study, at about 1.5 cm^{-1} resolution, a small shoulder is observed on the high frequency side of the peak. At a resolution of 0.4 cm^{-1} the shoulder becomes an incompletely resolved peak at 1270 cm^{-1} , but the low energy at this resolution necessitates the use of high gain settings, long time constants and exceptionally slow scan speeds and, consequently, the spectra have much higher noise levels than would normally be acceptable. Figure 15 shows a smoothed drawing of the band and is based on many high

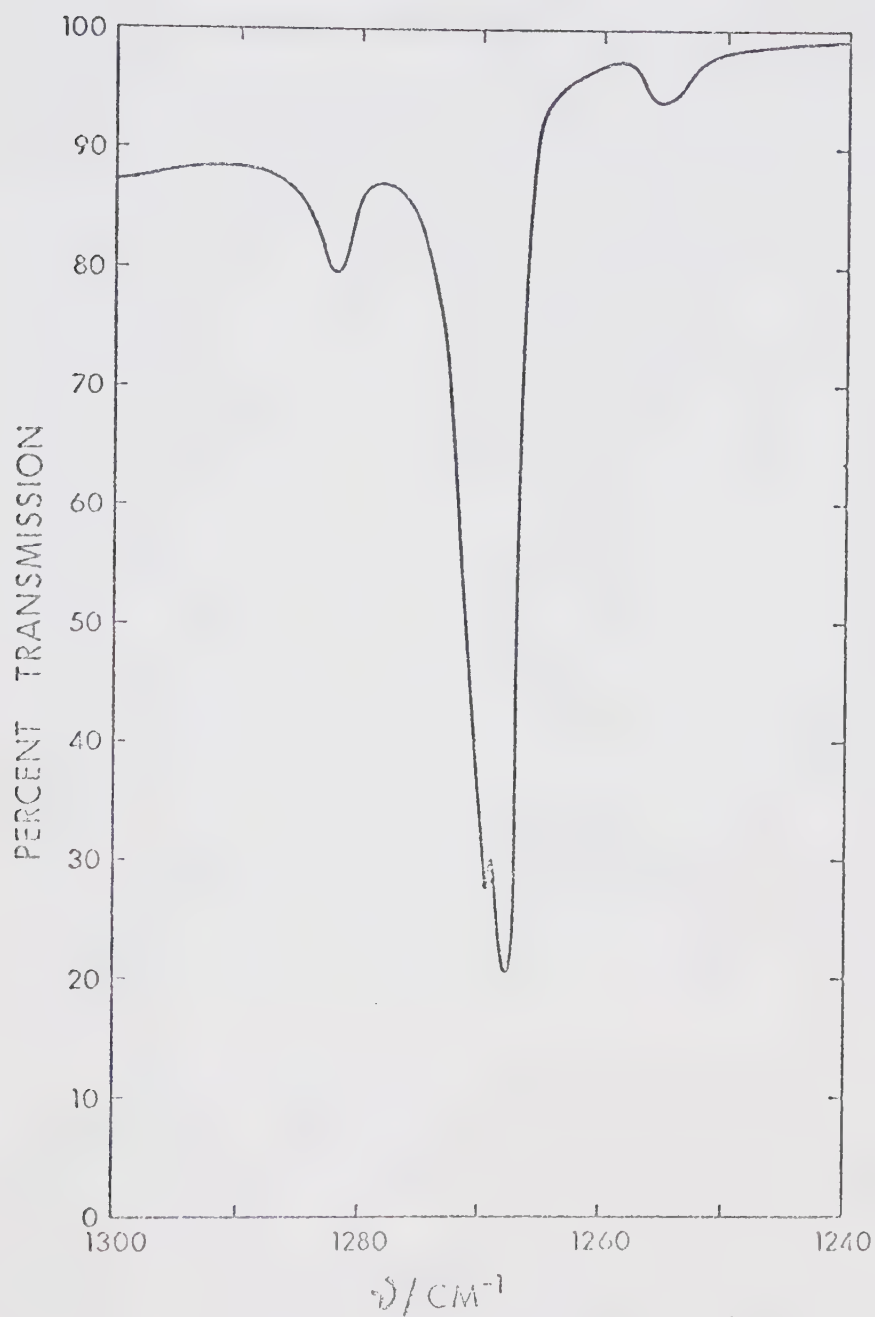


FIGURE 15. Absorption by ethylene oxide in ethylene oxide hydrate at 100°K. The instrumental resolution was 0.4cm^{-1} and the noise has been smoothed to show only the reproducible features.

resolution studies on different samples. From these studies it seems clear that the inherent line width of the components prevents further resolution. The half-width of the doublet is only about 4cm^{-1} . Two very weak peaks are also observed, on either side of the main absorption, at about 1255 and 1282cm^{-1} . The relative absorbances of all these four features were measured from the spectra with lower noise levels. No significant differences were observed between samples prepared by different methods. The absorbances of the 1255 , 1270 and 1282cm^{-1} peaks were, respectively, about 3, 58 and 7% of the main 1268cm^{-1} peak absorbance, but the variation between different mulls, even of the same sample, could be at least $1/3$ of these values. These large variations were probably due to the difficulties involved in obtaining good spectra and to the overlapping of the peaks.

The two weak guest absorptions in the region 1110 to 1160cm^{-1} are shown in Figure 14a. They occur in the hydrate and deuterate at about 1123 and 1147cm^{-1} but are partially obscured by all three mulling agents. In the figure the dashed line indicates the approximate hydrate absorption resulting from subtraction of a weak propylene peak. Owing to the weakness of these absorptions the exact shape of the bands is uncertain, and any weak shoulders present would probably not have been detected.

Below 1000cm^{-1} the deuterate has two clearly observable ethylene oxide absorptions, both with high frequency shoulders, as shown in curve a of Figure 16. The band at 872cm^{-1} is the strongest ethylene oxide absorption in the deuterate spectrum and has an unresolvable shoulder at 881cm^{-1} . The halfwidth of the overall band is about 15cm^{-1} . The feature at 805cm^{-1} with a shoulder at about 808cm^{-1} is much weaker and the combined band has a halfwidth of approximately 8cm^{-1} . The weak Freon 13 absorption in this region makes the study of the shoulder difficult, but the probable deuterate absorption is shown in Figure 16 by a dashed line. It was also possible to observe these bands in samples in which the mulling agent had evaporated, although the noise level and background transmission were poor. The bands appeared to increase in breadth when the sample was warmed by about 70°C , and they became narrower as it was recooled, although they did not return to the exact shape exhibited when the mulling agent was first removed. This apparent discrepancy may have been due to poor temperature control because of inadequate heat transfer.

In the hydrate the ν_R absorption occurs between 650 and 1000cm^{-1} and is rather unusual in shape by comparison with that of the deuterate or ice I, as shown in curve a of Figure 9. It is clearly influenced by the presence of ethylene oxide absorption but the band is not a simple

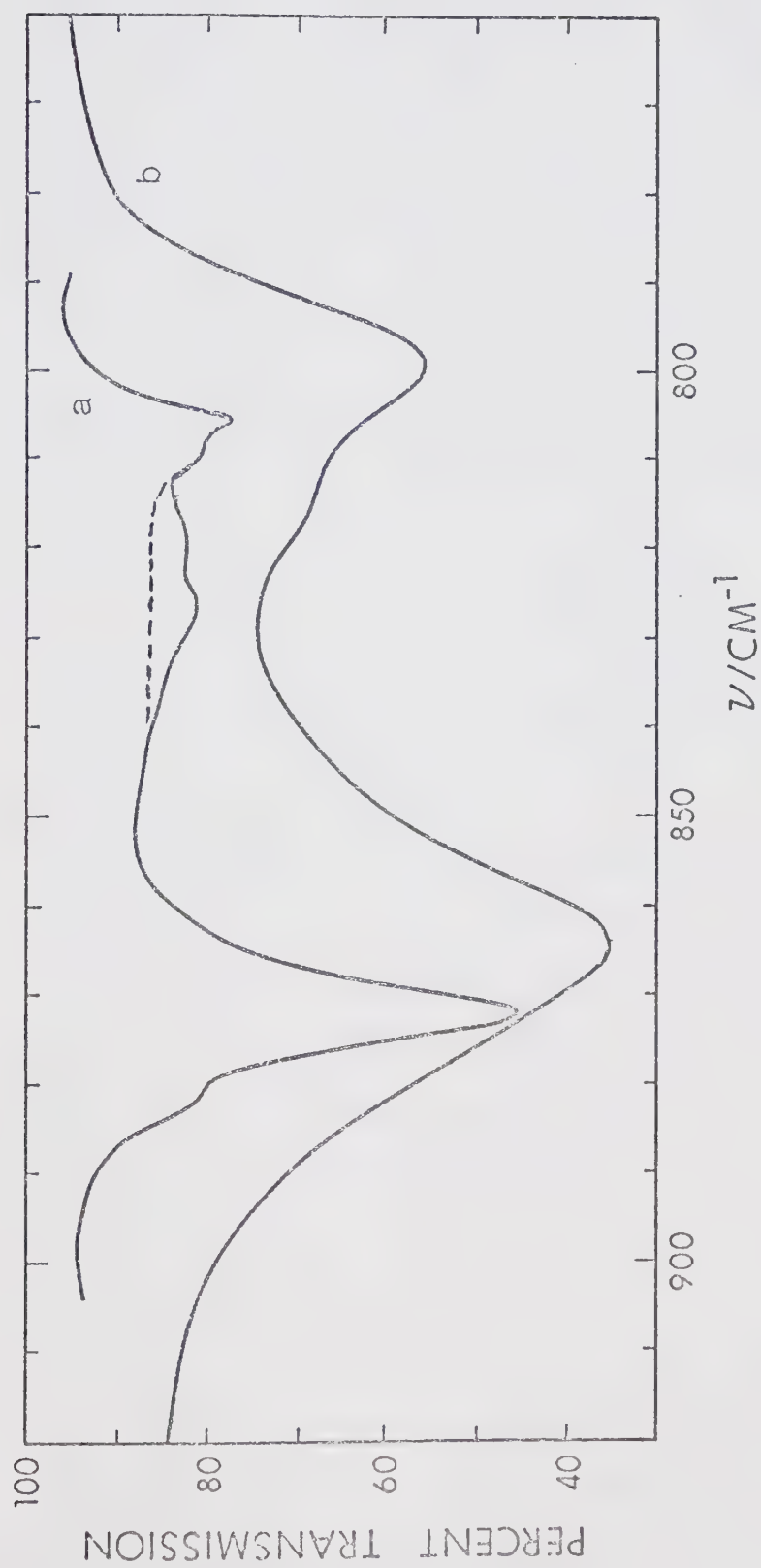


FIGURE 16. Absorption by ethylene oxide in ethylene oxide deuterate at 100°K (curve a) and in liquid ethylene oxide at 210°K (curve b).

superposition of the ethylene oxide peaks and the $\nu_R(\text{H}_2\text{O})^{122}$ band of ice. In particular, the steep rise at 864cm^{-1} and the shoulder at 890cm^{-1} do not correlate with the ethylene oxide absorption in the deuterate. A few other very weak features were occasionally observed in the clathrate spectra but these were not reproduceable.

No clear experimental evidence of the absorption due to the intermolecular vibrations of the guest molecule was obtained but arguments that lead to a tentative assignment of this absorption are presented in section 5.2.

Before an assignment of the absorption by the ethylene oxide guest molecules in the hydrate can be made, it is first necessary to briefly discuss the stoichiometry of the samples used. Glew and Rath (82) have shown that the stoichiometry of the hydrate varies slightly according to the composition of the solution from which it is crystallized, and to the temperature of formation. In particular samples grown from a 7 mole percent solution of ethylene oxide in water have a unit cell formula of $6.53\text{C}_2\text{H}_4\text{O} \cdot 0.46\text{H}_2\text{O}$ and contain 12.4 mole percent of ethylene oxide, whereas a 13 mole percent solution yields a hydrate of composition $6.7\text{C}_2\text{H}_4\text{O} \cdot 0.46\text{H}_2\text{O}$, which contains 12.7 mole percent of ethylene oxide, if the samples are formed at 6.5°C .

Samples prepared by method 3 were grown from solutions containing between 12 and 13 mole percent of ethylene oxide at about 5°C and the product should therefore be both homogeneous and uncontaminated by mother liquor. All

the tetrakaidecahedra and about 40% of the pentagonal dodecahedra should be occupied in these samples. The stoichiometry of samples grown by method 1 is less certain. However, in all preparations at least 80% of the solution solidified at about 5°C, and so the initial solution must have contained at least 7 mole percent of ethylene oxide. But, unless this solution were 12.7 mole percent, the composition of the mother liquor would change as crystallization proceeded and a non-homogeneous sample would result. The average stoichiometry would be about $6.4\text{C}_2\text{H}_4\text{O} \cdot 0.46\text{H}_2\text{O}$ and the grinding process should overcome any gross inhomogenities in the sample. Hence on the average from 20 to 40% of the pentagonal dodecahedra, and all of the tetrakaidecahedra should be occupied by ethylene oxide molecules in samples prepared by method 1. No convenient technique was found for measuring this stoichiometry. Unfortunately our X-ray photographs could not be used for this purpose because, as the work of McIntyre and Peterson (83) shows, the lattice parameters for samples within our composition range are almost identical at -150°C. In conclusion, the intensity of absorption by guest molecules in pentagonal dodecahedral cages should be about 10% of the total guest molecule absorption. At best, this intensity may vary by a factor of two between samples prepared by different techniques. It is not, therefore, surprising that no such effect was identified.

4.4 Assignment of Intramolecular Modes of Ethylene Oxide.

This assignment will be made by discussing all the information available on the spectra of gas, liquid and solid ethylene oxide, together with the three most recently published assignments. Where necessary detailed spectra, obtained in this study, of the appropriate spectral regions will be presented to illustrate the arguments. When this work was carried out the infra-red spectrum of liquid ethylene oxide had not been reported but the frequencies have since been tabulated (217). However, no picture of the spectrum has been published, and no halfwidths were discussed. Figure 17 shows the spectrum of liquid ethylene oxide at about -65°C .

Ethylene oxide has seven atoms and therefore fifteen fundamental intramolecular vibrations. These vibrations form the representation $5A_1 + 3A_2 + 4B_1 + 3B_2$ under the point group C_{2v} . The A_2 vibrations are the only infra-red inactive vibrations. A study of the symmetry of the internal coordinates, assuming that the ring angles and one angle around each carbon atom are redundant, shows that the internal coordinates form the representations shown in Table III.

The most recent assignments are by Lord and Nolin in 1956 (218), Potts in 1964 (205) and Aleksanyan and co-workers in 1971 (217). Lord and Nolin (218) studied the infra-red spectra of gaseous ethylene oxide and

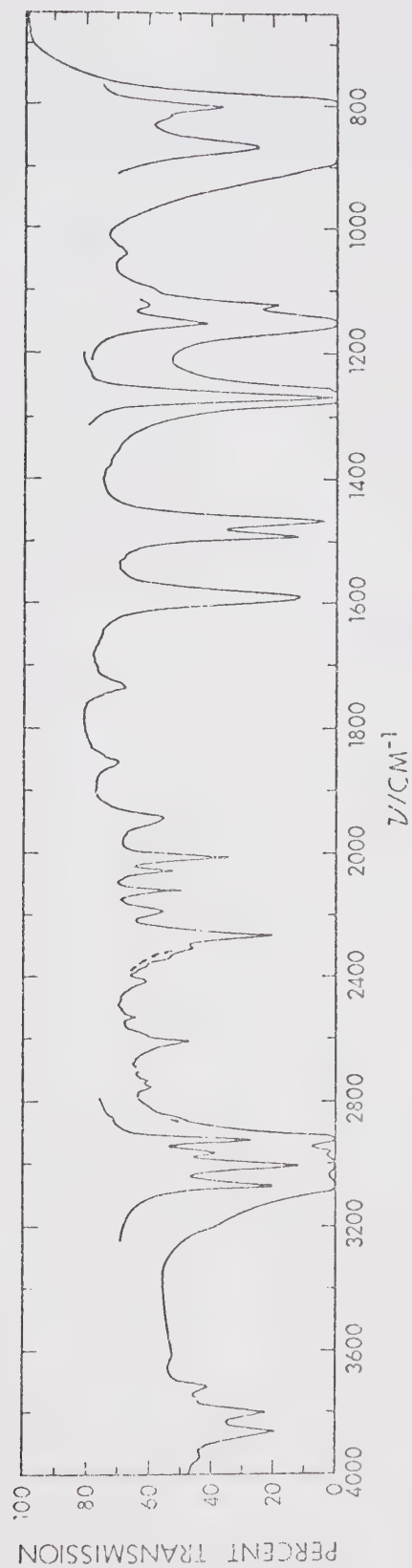


FIGURE 17. Mid-infrared spectrum of liquid ethylene oxide at about 210°K.

TABLE III. REPRESENTATIONS FORMED BY THE INTERNAL
COORDINATES OF ETHYLENE OXIDE IN THE POINT GROUP C_{2v} .

C-H stretch	$A_1 + A_2 + B_1 + B_2$
CH ₂ deformation	$A_1 + B_1$
CH ₂ wag	$A_1 + B_1$
CH ₂ twist	$A_2 + B_2$
CH ₂ rock	$A_2 + B_2$
Ring vibration	$2A_1 + B_1$
Total	$5A_1 + 3A_2 + 4B_1 + 3B_2$

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ethylene oxide- d_4 at rather low resolution, together with Raman spectra of the two liquids, whilst Potts (205) carried out infra-red studies on ethylene oxide and ethylene imine in the gaseous state and in solution. The Russian researchers (217) studied ethylene oxide- h_4 and $-d_4$. They reported the Raman spectra of the liquids, and infra-red spectra of the gas and liquid phases and of solid samples formed by freezing the liquid. These had monocrystalline regions which were suitable for polarization studies. The three assignments, using gas phase frequencies except where indicated, are shown in Table IV. The frequencies of Lord and Nolin (218) are probably the less accurate because of their lower resolution. Condensed films of ethylene oxide (219) and ethylene oxide in an argon matrix (220) have been studied by Le Brumant using infra-red spectroscopy. He also reported together the Raman spectra of the liquid and solid ethylene oxide (221). Le Brumant ignored factor group splitting in his assignment of the spectra of the solid and polarization studies have led Aleksanyan and co-workers (217) to interpret at least one of the features assigned by Le Brumant to a fundamental as a factor group allowed or Davydov component.

Several inconsistencies exist in the literature assignments shown in Table IV. The A_1 CH stretching frequency has not been clearly located, and two assignments make it degenerate with the B_1 CH stretch. The A_1 CH_2

TABLE IV. LITERATURE ASSIGNMENTS OF THE VIBRATIONAL
FREQUENCIES IN CM⁻¹ OF ETHYLENE OXIDE.

	<u>VIBRATION NUMBER AND</u> <u>APPROXIMATE FORM</u>	<u>REF.</u> <u>218</u>	<u>REF.</u> <u>205</u>	<u>REF.</u> <u>217</u>
A ₁	1 CH stretch	3005 R.	(~3006)	3006
	2 CH ₂ deformation	1490	1497.5	1496
	3 Ring breathe	1266	1270.5	1269
	4 CH ₂ wag	1120 R.	(~1130)	1123 R., L.
	5 Ring deformation	877	877	879
A ₂	6 CH stretch	3063 R.	(~3065)	3065
	7 CH ₂ twist	(1345)	(~1300)	1046 S.
	8 CH ₂ rock	807 R.	(~860)	818 L., S.
B ₁	9 CH stretch	3019	3006	3006
	10 CH ₂ deformation	1470	1471.5	1474
	11 CH ₂ wag	1153	1151	1150
	12 Ring deformation	892	(~890)	876 S.
B ₂	13 CH stretch	3079	3065	3065
	14 CH ₂ twist	1143	1142.0	1141
	15 CH ₂ rock	821	821.5	822

The abbreviations L., S., R., indicate that the assignment was based on infra-red studies of the liquid, or solid, or on Raman liquid studies respectively.

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wagging frequency has not been determined for the gas and two assignments used the polarized Raman liquid frequency at about 1120cm^{-1} whilst Potts (205) locates it at about 1130cm^{-1} . The B_1 ring deformation frequency has been assigned at 892cm^{-1} (218), about 890cm^{-1} (205) and, on the basis of the solid spectrum, at 876cm^{-1} (217). The higher resolution spectra of the present work show clearly that the feature at 890cm^{-1} (205, 218) is part of a B-type band, and should not be assigned to a distinct fundamental. Finally, the A_2 vibrations are only clearly seen in the infra-red spectrum of the solid (217) and, hence, the earlier assignments of these modes (205, 218) are suspect. Unfortunately, only a few of the authors show spectra and these generally lack adequate detail. For these reasons detailed infra-red studies of the spectra of gaseous, liquid and solid ethylene oxide were carried out together with a Raman study of liquid ethylene oxide. The frequencies are reported in Table V. The band shapes of the gas phase spectra were studied at about 0.8cm^{-1} resolution, and when clearly recognizable, are described as A, B or C-type (222) in Table V. Ueda and Shimanouchi (222) have calculated the approximate band contours in terms of two parameters, x and y , related to the moments of inertia. Using the moments of inertia of Cunningham and co-workers (143), ethylene oxide is calculated to be of Type 23 of reference 222 with 100 frequency divisions (222) being equal to about 64cm^{-1} .

TABLE Va. FREQUENCIES IN CM^{-1} OF FEATURES OBSERVED IN THE
 INFRA-RED SPECTRUM OF GASEOUS ETHYLENE OXIDE AT 300°K .

3094	br.		2138	w.	B	1168	peak	
3065.2	Q	C	2088	Q w.		1160.1	dip	
3061	Q w.		~2024	Q w.		1154.5	peak	
3057	dip		1934	Q w.		1150.6	Q	
3035	} plateau		1839	Q w.		1148.4	s.dip	
3022			1756	w.peak		1144.1	sh.	
3018	dip	B?	1751	dip	} B	1142.0	Q	
3014	w.peak		1747	w.peak		1133.8	peak	
3005.9	Q s.	A	1735	w.?		1127.6	sh.	
2999	w.peak		1718	br.w.		1121	plateau	
2992	} plateau		1701	blip		1034	w.peak?	
2984			1697	blip		1032	dip?	
2975	w.sh.?		1686	w.peak		1030	w.peak?	
2969	dip		1648	Q w.		900	} plateau	
2964	} plateau		1643.1	Q m.		892		
2947			1636	Q w.		882.0	Q" s.	} B
2930.1	Q		1626	Q w.		876.9	dip	
2923	w.peak?		1617	w.peak		~872.1	Q' s.	
2917.5	Q		1502	Q"		864.5	dip	
2910	sh.?		1498.4	dip	} B	~855	plateau	
2852	w.peak		1493	Q'		844	dip	
			1471.9	Q m.	A	839.4	sh.	
2315	Q w.		1457	Q w.		821.2	Q	
2306	Q w.		1419	Q w.		816	} w.br.peak	
2182	Q w.		1274.8	Q" s.		808		
2173	Q w.		1270.3	dip	} B			
			1264.9	Q' s.				

TABLE Vb. FREQUENCIES IN CM^{-1} OF FEATURES OBSERVED IN THE
INFRA-RED SPECTRUM OF LIQUID ETHYLENE OXIDE.

<u>THIS WORK</u> <u>210°K</u>		<u>REF. 217</u> <u>180°K</u>	<u>THIS WORK</u> <u>210°K</u>		<u>REF. 217</u> <u>180°K</u>
3940	w.		2123	w.	
3859	w.		2061	w.	
3800	w.		2015	w.	
3717	w.		1945	w.	
3072	s.	3071 s.	1854	w.	
~3014	sh.		1733	br.v.w.	
3003	s.	3001 s.	1591	m.	
2961	s.	2960 m.	1492	m.	
2922	s.	2920 s.	1468	m.	1466 s.
2755	w.				1457 sh.
2737	w.		1268.5	v.s.	1265 v.s.
2703	w.sh.?		~1255	v.w.sh.?	1256 w.sh.
2610	w.		1151	m.	1151 m.
~2590	v.w.sh.		1124	w.	1122 w.
2531	w.		1038	v.w.	1033 v.w.
2417	w.		864	v.s.	865 v.s.
2306	sh.		815	sh.	818 v.w.
2267	w.		799	s.	799 s.
2191	w.				

TABLE Vc. FREQUENCIES IN CM^{-1} OF FEATURES OBSERVED IN THE
INFRA-RED SPECTRUM OF SOLID ETHYLENE OXIDE.

THIS WORK 100°K	REF. 219 90°K	REF. 217 90°K	THIS WORK 100°K	REF. 219 90°K	REF. 217 90°K
3937 v.v.w.			2299 v.w.		
3893 v.w.			2282 sh.?		
3858 w.			2275 sh.	2274	
3834 v.v.w.			2268 w.	2266	
3820 v.v.w.			2207 w.	2205	
3792 w.			2196 w.	2195	
3703 v.v.w.			2116 w.	2113	
3074 s.	3073	3074	2084 v.v.w.?		
3064 s.	3061	3062	2062 v.v.w.?		
3052 sh.?	3050	3052	2056 v.w.	2054	
	3038		2019 v.v.w.		
3026 w.sh.	3023		2012 v.v.w.		
3008 s.	3004	3005	1950 w.		
2998 s.	2994	2996	1868 v.w.		
2965 m.			1724 v.w.		
2951 m.		2950		1588	
2916 s.	2915	2916	1584 m.	1583	1582
2905 sh.	2903	2905			1556
2857 v.w.			1496 w.	1494	1494
2848 v.w.?			1482 w.	1480	1480
2747 v.w.			1468 m.	1467	1467
2614 w.	2615		1462 w.	1459	1460
2601 w.	2599		1266 v.s.	1265	1267
2576 v.v.w.?			1255 m.	1253	1253
2527 v.w.	2526		1169 m.	1169.5	1170
2421 v.w.			1167 sh.	1166.5	1166
2367 v.w.			1161 m.	1160.5	1161
2320 w.			1147 s.	1147	1147

TABLE Vc. Continued.

<u>THIS WORK</u> <u>100°K</u>	REF. 219 <u>90°K</u>	REF. 217 <u>90°K</u>	<u>THIS WORK</u> <u>100°K</u>	REF. 219 <u>90°K</u>	REF. 217 <u>90°K</u>
1119 v.w.		1119	837 v.v.w.	836	838
		1117	826 v.v.w.	825	825
1047 w.	1046	1046	818 m.	818	818
~876 sh.	873	876	799 s.	795.5	798
860 br.v.s.	857	860	795 sh.	793	794
		854	785 v.w.	783.5	783

TABLE Vd. FREQUENCIES IN CM^{-1} OF FEATURES OBSERVED IN THE
RAMAN SPECTRUM OF LIQUID ETHYLENE OXIDE.

<u>THIS WORK</u> <u>300°K</u>	<u>DEPOLARIZATION RATIO</u>	<u>REF.</u> <u>218</u>	<u>REF.</u> <u>221</u>
3079 v.w.sh	not measurable		
~3061 m.	~0.75	3063	3063
3055 v.w.sh.	not measurable		
3009 s.	< 0.05	3005	3011
2960 s.	< 0.05	2961	2963
2915 s.	< 0.05	2916	2919
1492 m.	~0.1	1490	1494
1468 w.	0.72		1472
1268 v.s.	< 0.05	1266	1271
1255 v.w.sh.	not measurable		
1151 w.	0.72	1150	1156
1121 m.	< 0.05	1120	1124
867 m.	0.65	867	868
811 ? } br.m.	0.74		~813
803 }	0.76	807	804

The explanation of the abbreviations for all parts of Table V is: v.= very; s.= strong; m.= medium; w.= weak; sh.= shoulder.

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Since the intermediate moment of inertia, I_B , lies along the two fold axis, an A_1 vibration yields a B-type band with two broad peaks, Q' and Q'' about 12cm^{-1} apart, and a steep dip in between them. The B_1 and B_2 vibrations have their transition moments in, and out of, the plane of the ring, respectively, and yield A- and C-type band contours, respectively. Both have sharp, strong Q branches and weak, broad P and R branches. Compared to an A-type band the C-type band has a more prominent Q branch and the P and R branches show more fine structure. The P and R branches peak about 27cm^{-1} away from the Q branch for a C-type band and for an A-type band the analogous separation is about 20cm^{-1} .

The CH stretching vibrations absorb at frequencies above 2980cm^{-1} and several strong overtone and combination bands are observed just below this frequency (205, 218). The B_1 and B_2 vibrations are unambiguously assigned at 3005.9 and 3065.2cm^{-1} . Subtraction of the P branch, indicated by the dotted line in Figure 18, which is the mirror image of the R branch of the 3065.2cm^{-1} band, gives the dashed line in Figure 18. The shape of the residual curve indicates the presence of a B-type band at 3018cm^{-1} . This assignment is strengthened by the existence of the steep rise above 3018cm^{-1} , which only appears to occur in the spectrum of gaseous ethylene oxide in B-type bands, and by the fact that the two peaks are about 10cm^{-1} apart

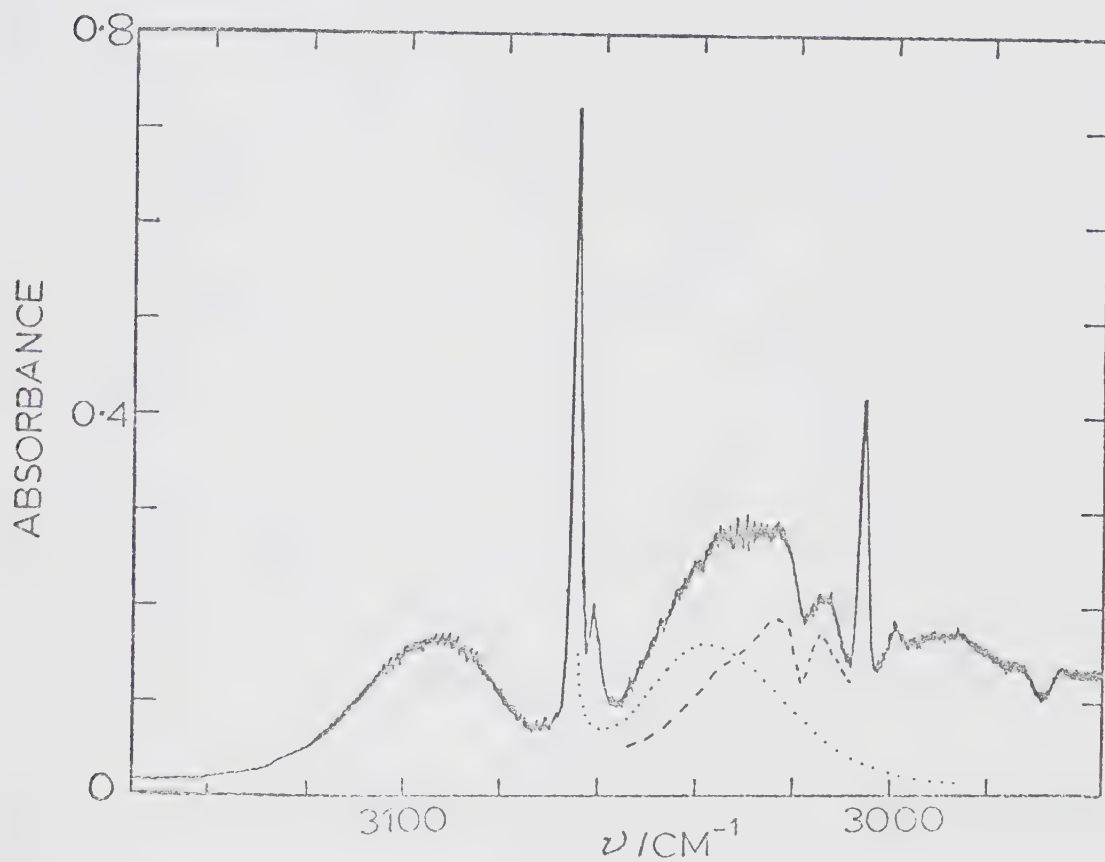


FIGURE 18. Absorption by ethylene oxide gas at 300°K. The dotted line indicates the estimated P branch while the dashed line indicated the band shape remaining after subtraction of this P branch.
Gas Pressure was 17 Torr.

and are similar in breadth to those observed for the isolated B-type band at 1270.3cm^{-1} . The A_1 CH stretching vibration is therefore assigned at 3018cm^{-1} in the gas phase. The features at 3061 and 2999cm^{-1} are then presumably due to hot bands or isotopic impurity bands. An alternative, but less likely, assignment is that the two peaks on either side of the 3005.9cm^{-1} Q branch, at 3014 and 2999cm^{-1} , are the Q" and Q' branches of the B band. This assignment, which was adopted by Potts (205), would not explain the sharp rise in the absorption above 3018cm^{-1} . Further the liquid spectrum, curve b of Figure 13, shows a slight but definite shoulder at roughly 3014cm^{-1} on the side of the 3003cm^{-1} peak, indicating the existence of two absorptions in this region. The Raman spectrum provides no evidence relevant to this assignment because the spectrum is dominated by intense polarized lines, and it is not possible to tell whether the features seen under perpendicular polarization are the depolarized components of these lines or are due to non-totally symmetric modes. In the hydrate two sharp absorptions are seen at 3009 and 2998cm^{-1} , as shown in curve a of Figure 13, and these are, therefore, assigned to the A_1 and B_1 CH_2 stretching frequencies respectively. The B_2 vibration is at 3066cm^{-1} and the A_2 vibration is not observed in the hydrate. There is no indication of factor group splitting for these vibrations in the clathrate.

The ethylene oxide absorptions in the hydrate and deuterate at about 1491 and 1467cm^{-1} , shown in Figure 14b, are clearly caused by the A_1 and B_1 CH_2 deformations respectively. The absorption is sharp, and there is no reliable indication of fine structure. The assignment is in agreement with the observation that the 1492cm^{-1} Raman peak in the liquid spectrum is polarized.

Figure 15 shows the absorption of the ethylene oxide in the hydrate at 100°K in the region 1240 to 1300cm^{-1} smoothed to eliminate background noise. Four features are observed at 1255 , 1268 , 1270 and 1282cm^{-1} . Clearly the central band is associated with the A_1 symmetric ring vibrations but the presence of four features makes the assignment difficult. Samples prepared by different techniques failed to show any significant differences in the relative intensity of these four features. These samples would be expected to have different stoichiometries and, therefore, different occupancies of the dodecahedral cages. Hence none of these features can be assigned to absorption by guest molecules in these cages. However, the evidence is not definitive because the stoichiometries of the samples were not measured, and because the accuracy of the relative absorbances of the four features is low. The two weak features are about 13cm^{-1} away from the band centre and could be sum and difference bands with a low frequency vibration. However, Aleksanyan and co-workers

(217) have assigned a feature at about 1255cm^{-1} in the spectra of the solid and liquid phases of ethylene oxide to absorption by $\text{C}^{12}\text{C}^{13}\text{H}_4\text{O}$ and this seems a more plausible assignment for the 1255cm^{-1} peak. Hence all four features must be assigned to absorption by the A_1 symmetric ring vibration with the speculation that some of the features are due to guest molecules in different environments.

The infra-red spectrum of gaseous ethylene oxide in the region 1100 to 1200cm^{-1} , shown in Figure 19, has been interpreted in terms of one A and one C-type band only (205, 217, 218). The intensely polarized Raman line at 1122cm^{-1} has been taken as the frequency of the A_1 vibration (217, 218) or used to estimate the gas phase frequency (205), but no corresponding B-type band has been located in the gas phase spectrum. The unusual shape of both Q branches led to the idea that a B-type band might be located at about 1148cm^{-1} with the 1154.5 peak and the 1144.1cm^{-1} shoulder forming the Q" and Q' branches. In Figure 19 the dotted line shows a typical B-type band, copied from the 1270.3cm^{-1} band and positioned to coincide with the 1154.5cm^{-1} peak. If this band is subtracted from the observed spectrum the curve shown in Figure 20 is obtained. This is clearly the superposition of an A-type and a C-type band at 1150.6 and 1142.0cm^{-1} respectively, together with a small contribution from the tail of the 1270.3cm^{-1} band. The R branches of the two bands overlap

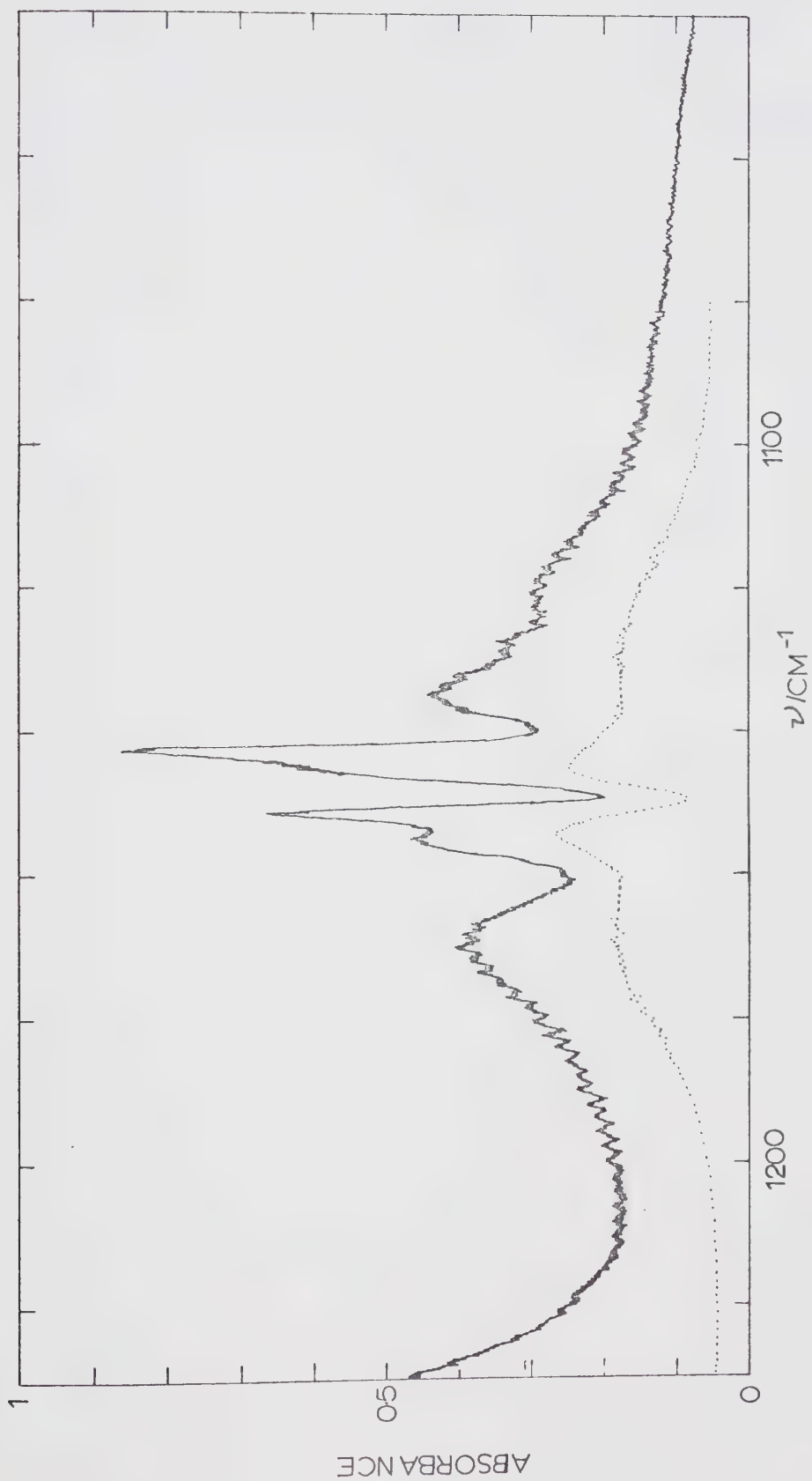


FIGURE 19. Absorption by ethylene oxide gas at 300°K and 300 Torr. The dotted line indicates the shape of a B-type band copied from the band at 1270.3cm^{-1} and 18 Torr.

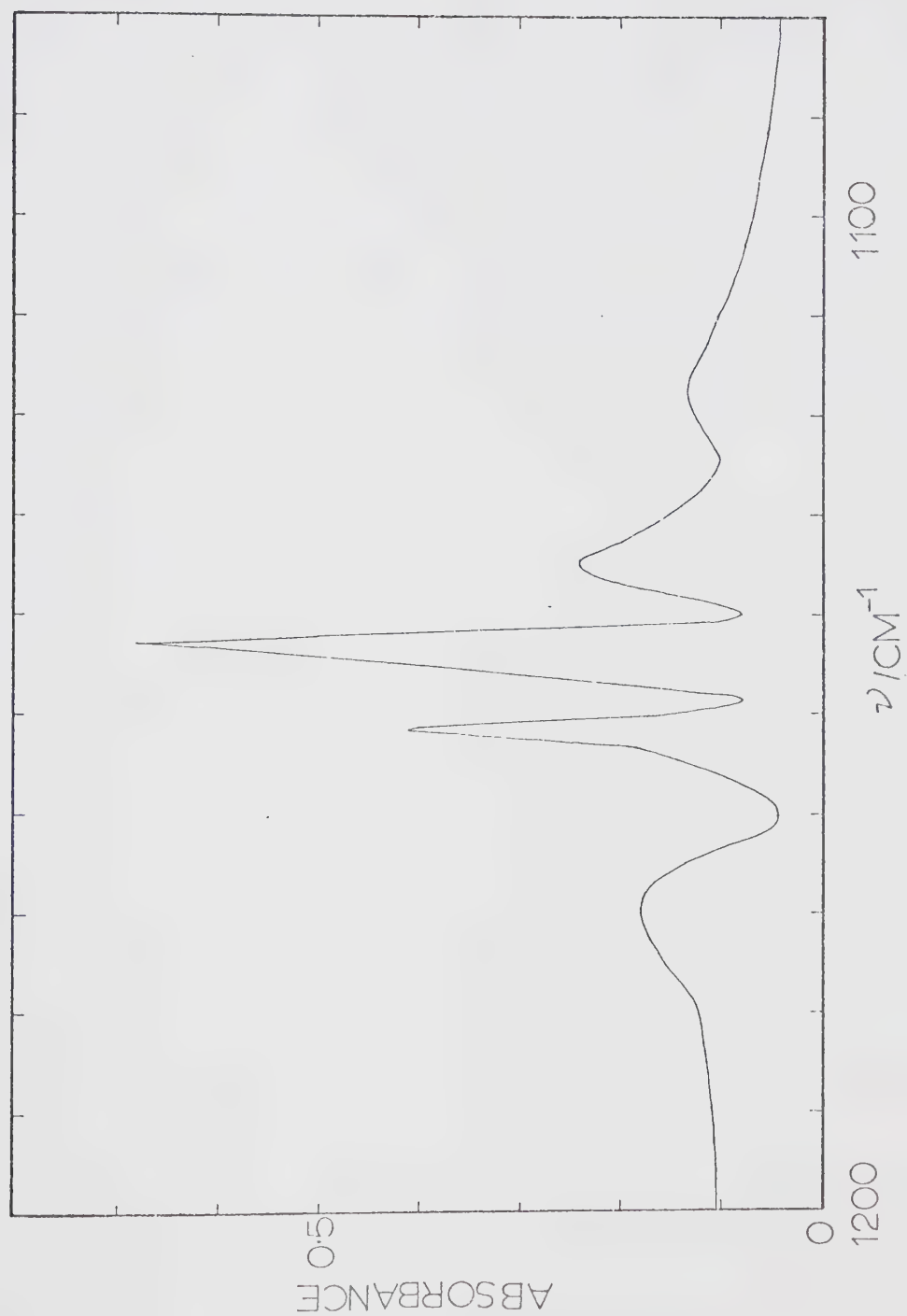


FIGURE 20. The band shape remaining after the dotted curve has been subtracted from the solid curve in Figure 19.

to give the peak at about 1170cm^{-1} whilst the P branch of the A band gives rise to the peak at about 1135cm^{-1} and the P branch of the C band causes the peak at about 1117cm^{-1} . Hence the A_1 wag is assigned at 1148cm^{-1} , the B_1 wag at 1150.6 and the B_2 twist at 1142.0 . An alternative assignment is to place the A_1 vibration at the dip at 1138cm^{-1} , but this would not explain the other features so readily and hence it will not be discussed further. The infra-red and Raman spectra of liquid ethylene oxide each show two bands, at about 1122 and 1151cm^{-1} . The low frequency Raman band is almost totally polarized and hence must be the A_1 wag. Therefore the 1151cm^{-1} band is due to both the B_1 wagging and the B_2 twisting vibrations. In the hydrate and deuterate the two bands at 1123 and 1147cm^{-1} are assigned in the same way. The frequency difference between the gas and condensed phases is the strongest argument against the assignment of the A_1 CH_2 wag at 1148cm^{-1} in the gas phase. However, quite large gas-liquid frequency shifts are observed for the bands between 800 and 900cm^{-1} , and therefore, this argument is not compelling.

The broad infra-red absorption by gaseous ethylene oxide which stretches from 780 to 940cm^{-1} is shown in Figure 21. It clearly contains a B-type band, the A_1 ring deformation, at 876.9cm^{-1} and a Q branch at 821.2cm^{-1} . However, the low frequency branch of the B-type band is

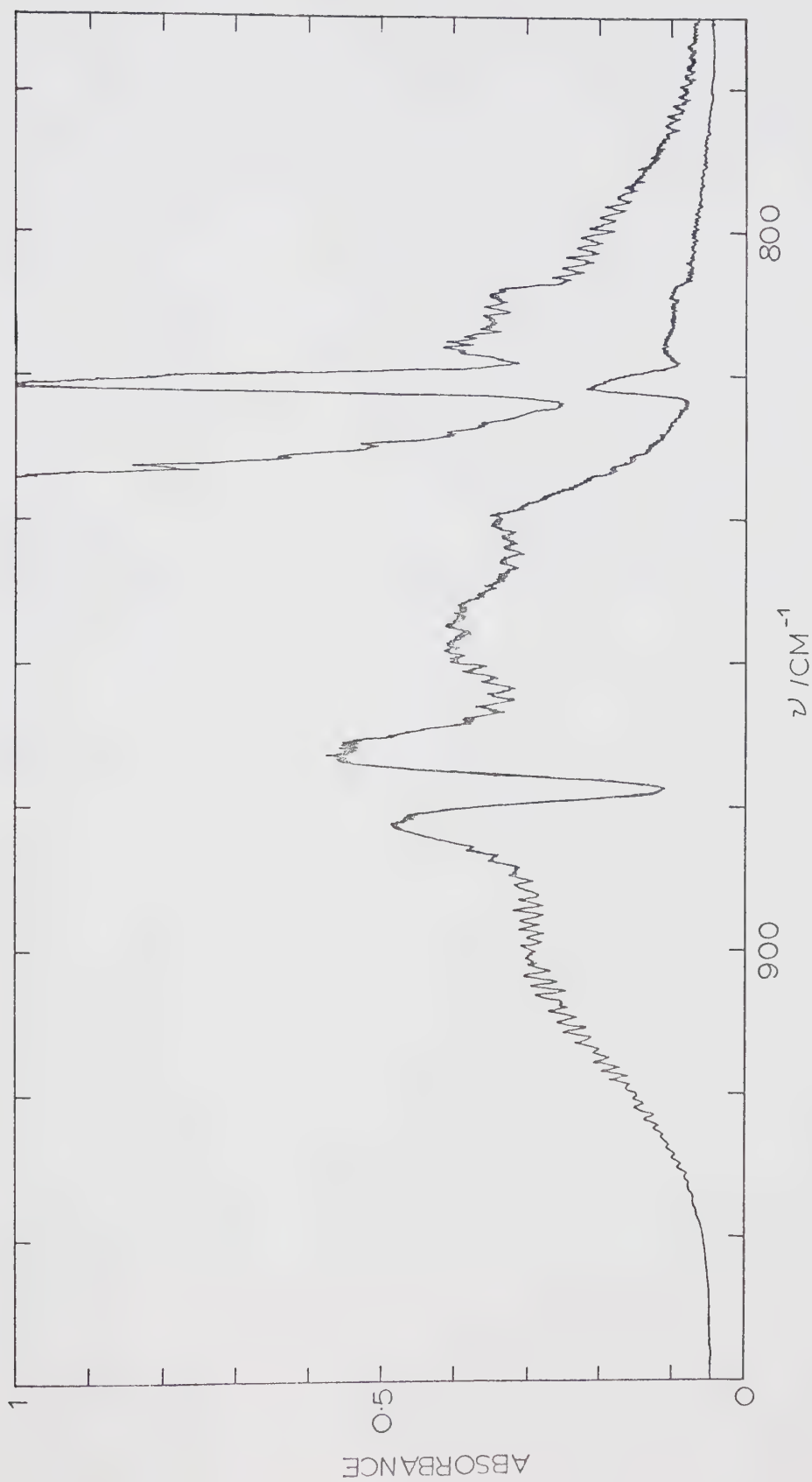


FIGURE 21. Absorption by ethylene oxide gas at 300°K.
Gas pressures were 17 and 87 Torr.

unusual in shape, the region between 825 and 875cm^{-1} has many features and the P branch, associated with the asymmetric Q branch at 821.2cm^{-1} , is steep-sided, as is clearly seen in the upper curve in Figure 21. The infrared spectrum of the liquid shows peaks at 864 and 799cm^{-1} with a shoulder at 815cm^{-1} . The 864cm^{-1} peak is unusually broad as seen in curve b of Figure 16. The Raman spectrum, shown in Figure 22, has depolarized peaks at 807 and 867cm^{-1} , with slight evidence for the doublet feature of the 807cm^{-1} peak listed by Le Brumant (221). Because the 867cm^{-1} peak is not strongly polarized it seems likely that more than one fundamental occurs in this region. This would be in agreement with the existence of a weak Q branch contributing to the low frequency peak of the B-type band at about 872cm^{-1} . This Q branch could be the B_1 ring vibration or the B_2 rock with a slight preference for the former assignment since the B_1 ring vibration in other three membered rings is usually observed at a frequency intermediate between the two A_1 ring vibrations (205, 223). The former assignment would also agree with Aleksanyan and co-workers (217) who assigned a band at 876cm^{-1} in the solid to this B_1 ring vibration. Hence the Q branch at 821.2cm^{-1} must be assigned to the B_2 rock and its unusual shape may be due to the tail of the 876.9cm^{-1} band and to band asymmetry. An alternative assignment of the B_1 ring vibration as the cause of the unusual shape of the peak at

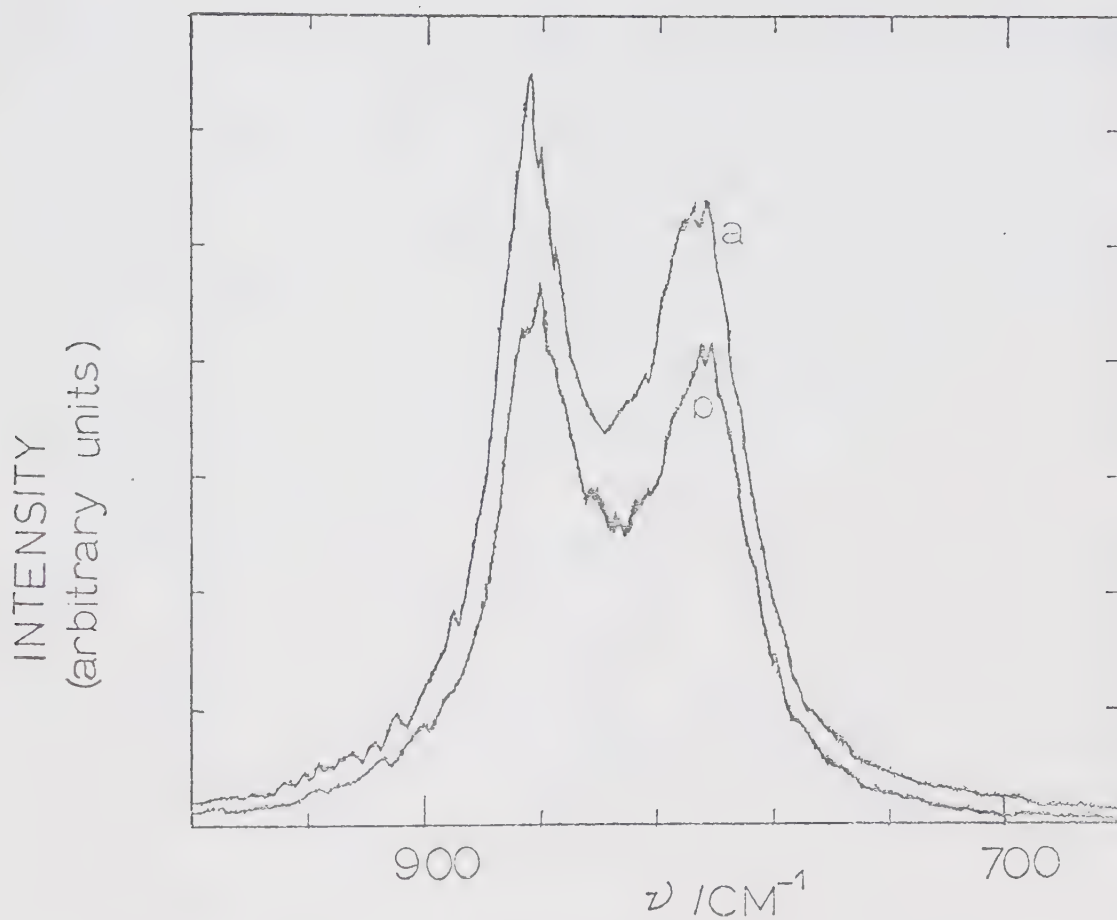


FIGURE 22. The Raman spectrum of liquid ethylene oxide at 300°K. Curve a was observed under parallel polarization while curve b was observed under perpendicular polarization.

821.2cm^{-1} is possible but all attempts to locate the frequency of this B_1 vibration by band contour analysis have been unsuccessful and the former assignment is preferred. The deuterate shows two peaks and two shoulders in this region, Figure 16. Accepting the initial gas phase assignment the features at 872 and 881cm^{-1} must be due to the A_1 and B_1 ring deformations whilst one of the features at 810 and 807cm^{-1} must be due to the B_2 rocking vibration. Perhaps the other feature can be assigned to the A_2 rock which has been assigned by Aleksanyan and co-workers (217) at 818cm^{-1} in the infra-red spectra of the solid. The feature observed by us at 815cm^{-1} and by the Russians (217) at 818cm^{-1} in the infra-red spectrum of the liquid has also been assigned to this vibration. Hence, the absorption at 810cm^{-1} in the deuterate is probably associated with the A_2 rocking vibration, and the more intense band at 807cm^{-1} is assigned to the B_2 rock.

The assignment of the ethylene oxide vibrations in the gas, liquid and clathrate phases is summarized in Table VI, using the frequencies obtained in this work. The only observed absorptions due to ethylene oxide that have not been discussed are the overtone and combination bands at 2914 , 2922 , 2958cm^{-1} . In the spectra of pure ethylene oxide numerous additional features were observed. The only attempt to assign any of these features dealt with the Q branches between 1600 and 1700cm^{-1} and the

TABLE VI. PROPOSED ASSIGNMENTS FOR FUNDAMENTAL ETHYLENE
OXIDE VIBRATIONS IN GAS, LIQUID AND CLATHRATE.

		<u>GAS</u>	<u>LIQUID</u>	<u>CLATHRATE</u>
CH stretch	A ₁	3018	3014	3008
	A ₂	not observed		
	B ₁	3005·9	3003	2999
	B ₂	3065·2	3072	3069
CH ₂ deformation	A ₁	1498·4	1492	1491
	B ₁	1471·9	1468	1467
Ring vibration	A ₁	1270·3	1268	{ 1268 1270
	A ₁	876·9	864	{ 881
	B ₁	872	864	{ 872
CH ₂ wag	A ₁	1148	1124	1122
	B ₁	1150·8	1150	1147
CH ₂ rock	A ₂	not observed	815	810
	B ₂	821·2	799	807
CH ₂ twist	A ₂	not observed		
	B ₂	1142·0	1150	1147

- - - -

features between 1025 and 1050cm^{-1} . The assignment of the Q branches was unclear and because of the possible influence of very small concentrations of impurities no conclusions could be drawn. A strong band at 1045cm^{-1} occurs in the infra-red spectrum of the solid and has been assigned (217, 219) to the A_2 twist. Very weak features at 1033cm^{-1} in the liquid infra-red and Raman spectra and at 1029cm^{-1} in the infra-red spectrum of gaseous ethylene oxide were similarly assigned (217). These features were also observed in this work but the band in the gas phase spectrum cannot be an A_2 vibration and its origin is unknown.

CHAPTER 5. DISCUSSION.

5.1 Absorption by the Water Molecules.

The absorptions by the $\nu_{\text{OH}}(\text{H}_2\text{O})$, $\nu_2(\text{H}_2\text{O})$ and $\nu_{\text{R}}(\text{H}_2\text{O})$ modes in the hydrate, and their analogues in the deuterate, have the same general appearance as those seen for other phases primarily containing disordered water molecules: ices Ih, Ic, V and VI (176, 177, 200). The main factors influencing these absorptions have been discussed qualitatively by Bertie and Whalley (176). In particular, since there is no order in the hydrogen positions, there are no strict selection rules and all vibrations are in principle infra-red and Raman active. Further, at 77°K the most intense Raman bands in the $\nu_{\text{OH}}(\text{H}_2\text{O})$ and $\nu_{\text{OD}}(\text{D}_2\text{O})$ regions of the ice Ih spectrum are at 3085cm^{-1} and 2283cm^{-1} , respectively (224), and thus occur at frequencies well below the frequencies of maximum absorption in the corresponding broad, infra-red bands. In addition, the features in the Raman spectrum are much sharper than those in the infra-red spectrum. Hence, the relative intensities of the different crystal vibrations arising from the OH or OD stretching modes must vary considerably from one crystal vibration to another, and must differ markedly between the infra-red and Raman spectra. It is convenient, therefore, to regard the broad absorptions as being made up of a density of vibrational states curve multiplied by an intensity distribution function. This intensity

distribution function can be very asymmetric with respect to the band of frequencies resulting from particular modes, as must be the case for the $\nu_{\text{OH}}(\text{H}_2\text{O})$ and $\nu_{\text{OD}}(\text{D}_2\text{O})$ bands, at least in the Raman spectrum.

Early workers assigned the peak and two shoulders seen on the $\nu_{\text{OH}}(\text{H}_2\text{O})$ band in the infra-red spectrum of ice I to the symmetric, ν_1 , and asymmetric, ν_3 , stretching vibrations and to the overtone, $2\nu_2$, of the H-O-H angle deformation mode (225 - 227). There was also some discussion as to the relative locations of the ν_1 and ν_3 modes (225 - 227). Bertie and Whalley (176) pointed out that at least six spectral features (five infra-red and one Raman) arise from the $\nu_{\text{OD}}(\text{D}_2\text{O})$ vibrations, and therefore the true assignment must be more complicated. They also pointed out that, because of the disorder, the intermolecular coupling will cause not only the symmetric and asymmetric modes to each yield a broad band of crystal frequencies, but will also cause the two modes to couple when their frequencies are similar. Thus the density of states curve could contain many features. They, therefore, suggested (176) that the assignment of the three main features to ν_1 , ν_3 , and $2\nu_2$ is ambiguous and questionable, and that it is not necessary to invoke the appearance of $2\nu_2$ in this absorption, although it could contribute. Hence, the details of the form of the crystal vibrations which contribute to the spectra at the various frequencies

and the reasons for the features in the intensity distribution functions are unknown. Therefore, no detailed assignment of the $\nu_{\text{OH}}(\text{H}_2\text{O})$ and $\nu_{\text{OD}}(\text{D}_2\text{O})$ bands in ice I or in the clathrate can be made.

For many systems, more detailed assignments can generally be made by calculating a spectrum and refining the parameters until the observed and calculated spectra agree closely. In the case of systems which are mainly composed of disordered water molecules and which show very broad bands in their spectra, it seems likely that calculations will not yield a definitive interpretation until the same model is applied to the spectra of many such phases, because of the disorder and the possible complications arising from hydrogen bonding. These calculations have not been made and are not readily carried out. Therefore the discussion of the present work can only point out certain spectra-structure correlations that any such theory must explain. In the following discussion only the influence of the O-O hydrogen bond lengths in the various phases will be considered. Even with this simplification, the conclusions are limited. Therefore, there seems to be no justification for discussing in detail the influence of the O-O-O angles or the effect of other than nearest neighbours except to point out that the angles around each oxygen atom in the hydrate are not all tetrahedral, as they are in ice I, although the weighted

average is 109.6° , and that the arrangement of non-nearest neighbours is quite different from that in ice I.

In ice Ih all of the O-O bond lengths are very close to $2.75\overset{\circ}{\text{\AA}}$ at 100°K (182 - 185), while in the hydrate 52% of the O-O bonds are $2.75\overset{\circ}{\text{\AA}}_4$ long, 26% are $2.78\overset{\circ}{\text{\AA}}_9$ long and the remainder are either $2.74\overset{\circ}{\text{\AA}}_5$ or $2.82\overset{\circ}{\text{\AA}}_1$ long. These values for the hydrate were obtained from the values at -25°C (81) by allowing for the approximately 0.8% contraction between 248°K and 100°K indicated by the work of McIntyre and Peterson (83). A comparison of the $\nu_{\text{OH}}(\text{H}_2\text{O})$ bands, and also the $\nu_{\text{OD}}(\text{D}_2\text{O})$ bands, in the hydrate and in ice Ih shows that they are very similar, but the hydrate features are rather broader, causing this spectrum to resemble a poorly resolved spectrum of ice I. It is, therefore, reasonable to conclude that the main features of the hydrate and deuterate spectra are determined by the 52% of the O-O bonds that are $2.75\overset{\circ}{\text{\AA}}$ long, the same length as occurs in ice I. The breadth of the features would then be interpreted as arising mainly from the 26% of the bonds about $2.79\overset{\circ}{\text{\AA}}$ long with smaller effects caused by the remaining bonds. Phenomenologically the spectra and structures of the hydrate and ice Ih can be related in this manner. Such an interpretation also accounts for the identity of these bands in ice Ih and ice Ic, both of which contain only O-O bonds about $2.75\overset{\circ}{\text{\AA}}$ long (182 - 185). The rationalization of the shape and frequencies of the

$\nu_{\text{OH}}(\text{H}_2\text{O})$ and $\nu_{\text{OD}}(\text{D}_2\text{O})$ absorptions in ices V (177) and VI (200) is less easy, because they do not show one peak and two main shoulders, as do those of the hydrate, ice Ih and ice Ic. However, both ices V and VI contain a roughly equal distribution of O-O hydrogen bond lengths from $2.78\text{\AA}$ to $2.84\text{\AA}$ (166, 195) and it is, perhaps, not surprising that the absorption is shaped differently from that shown by the simpler structures. Further ices V and VI are partially ordered (166, 195) and this could well influence the spectra.

From theoretical considerations, one would expect the vibrations of the hydrogen atoms in the bonds of different lengths in the hydrate to have different frequencies, but to interact to yield crystal vibrations that simultaneously involve the atoms in non-equivalent bonds. Therefore, one would expect the density of O-H stretching vibrational states to be quite different in the hydrate and in ice Ih. One would also expect the intensity distribution function to differ significantly between the two phases. However, the experimental evidence indicates that, because a peak and two main shoulders are seen for both the hydrate and ice I, neither the density of states curve nor the intensity distribution function differ greatly between the two phases. However, it is just possible that the coincidence occurs that both differ significantly but that the differences in each one exactly cancel.

The most plausible explanation of these observations is that the random orientations of the water molecules causes the intermolecular coupling to vary from site to site in the lattice, and that the density of states curve, which results from the average over the whole crystal, is similar in both phases. Further, the intensity distribution function must result from some average of the effects of the disorder over the entire crystal, and the function appears to be insensitive to the structural differences that exist between the hydrate and ice Ih.

The $\nu_R(\text{H}_2\text{O})$ band in the infra-red spectrum of ice I extends from at least 1050 to 400cm^{-1} with the most intense absorption lying between 750 and 920cm^{-1} (176). In contrast, heat capacity measurements have shown that the contribution of $\nu_R(\text{H}_2\text{O})$ can be approximately represented as that of $3N$ vibrations each at 620cm^{-1} (228, 229). Hence, if the centre of gravity of the ν_R modes is at 620cm^{-1} , then the high frequency modes must absorb infra-red light much more strongly than the other modes and the intensity distribution function is necessarily very asymmetric with respect to the band of crystal frequencies. The close similarities between the $\nu_R(\text{D}_2\text{O})$ absorption in ice I and in the deuterate indicate that the clathrate also has a very asymmetric intensity distribution function.

A comparison of the structures of ices Ih (182 - 185), V (66) and VI (195) and ethylene oxide hydrate (81) shows

that there are 4, 14, 10 and 46 water molecules in their primitive unit cells. Because the $\nu_R(\text{H}_2\text{O})$ absorption bands of ice V and VI differ from that of ice I much more than does the analogous band of ethylene oxide hydrate, it is clear that the spectra are not seriously influenced by the size of the unit cell. Further, the phases contain 1, 4, 2 and 3 crystallographically non-equivalent water molecules, respectively, and it is clear that this factor does not influence the spectra appreciably. The absence of pronounced features in the ν_R band of ices I, V and VI and the deuterate makes it difficult to interpret these spectra in terms of O-O bond distances, but it does appear to be most probable that the density of states curve for rotational vibrations and the corresponding intensity distribution function are very similar in D_2O ice Ih and the deuterate in spite of the structural differences between these phases.

The shape of the $\nu_R(\text{H}_2\text{O})$ band in the hydrate is clearly affected by the presence of ethylene oxide absorptions in a manner which is not just a simple addition of intensities. These changes in shape indicate that coupling occurs between the $\nu_R(\text{H}_2\text{O})$ vibrations and the intramolecular ethylene oxide vibrations at about 870cm^{-1} . Such coupling may occur either through transition dipole-transition dipole interaction or via a mechanical resonance process through the intermolecular forces, and will be

discussed in the following section.

The conclusions derived from the similarities of the $\nu_R(D_2O)$, $\nu_{OH}(H_2O)$ and $\nu_{OD}(D_2O)$ bands in ice I and the hydrate presumably also apply to the ν_2 and $3\nu_R$, $\nu_2 + \nu_R$ bands because of their similarities in the two spectra.

Between 360 and 100cm^{-1} the hydrate and deuterate have broad absorption spectra with no particularly sharp features. The band shifts by 3% on deuteration, clearly indicating that the dominant absorption arises from the translational vibrations of the water molecules. However, the peak isotope shift is slightly less in the hydrate than it is in ice I, and this will be discussed later. The breadth of the band and the appearance of structure upon it clearly indicate that the water molecules are statically disordered at 100°K , thereby confirming the previous studies which were discussed in section 1.6.

Application of the theory for absorption by translational vibrations in orientationally disordered crystals (196) to ethylene oxide hydrate leads to the prediction that the spectrum is a superposition of broad absorption, arising from the random part of the dipole moment derivative, and sharp absorptions, arising from the average part of the dipole moment derivative, section 2.2. The broad absorption approximates the density of states weighted by frequency-squared while the sharp absorptions are due to transitions allowed under the factor group of

the diffraction space group, $Pm3n$, O_h^3 . Nine F_{1u} water translational modes are infra-red allowed by the hydrate diffraction symmetry, as compared with none in ice Ih or ice Ic (198). The absence of the predicted sharp features from the spectrum (Figure 7) must occur either because of errors in the theory or because μ_{ave} is very small or zero. The latter explanation seems the more probable and can be rationalized simply in the following way. For each crystallographically equivalent O-O hydrogen bond the hydrogen atom must be positioned either as $O-H\cdots O$ or as $O\cdots H-O$. The change in dipole moment when an $O-H\cdots O$ bond is stretched must roughly oppose that when an $O\cdots H-O$ bond is stretched, and for a totally disordered system of water molecules μ_{ave} must be very small. Support for the view that the theory is correct arises from studies of ice V and hexamethylenetetramine hydrate, both of which are partially ordered and show sharp features in their far infra-red spectra assignable to transitions allowed under the diffraction factor group (202). Because of the absence of diffraction factor group allowed transitions the hydrate spectrum arises from disorder allowed absorption and the curve shown in Figure 23, which presents a plot of the absorbance divided by the square of the frequency against frequency, approximates the density of states for the translational modes of the water. Figure 23 is not extended below 100cm^{-1} because of the

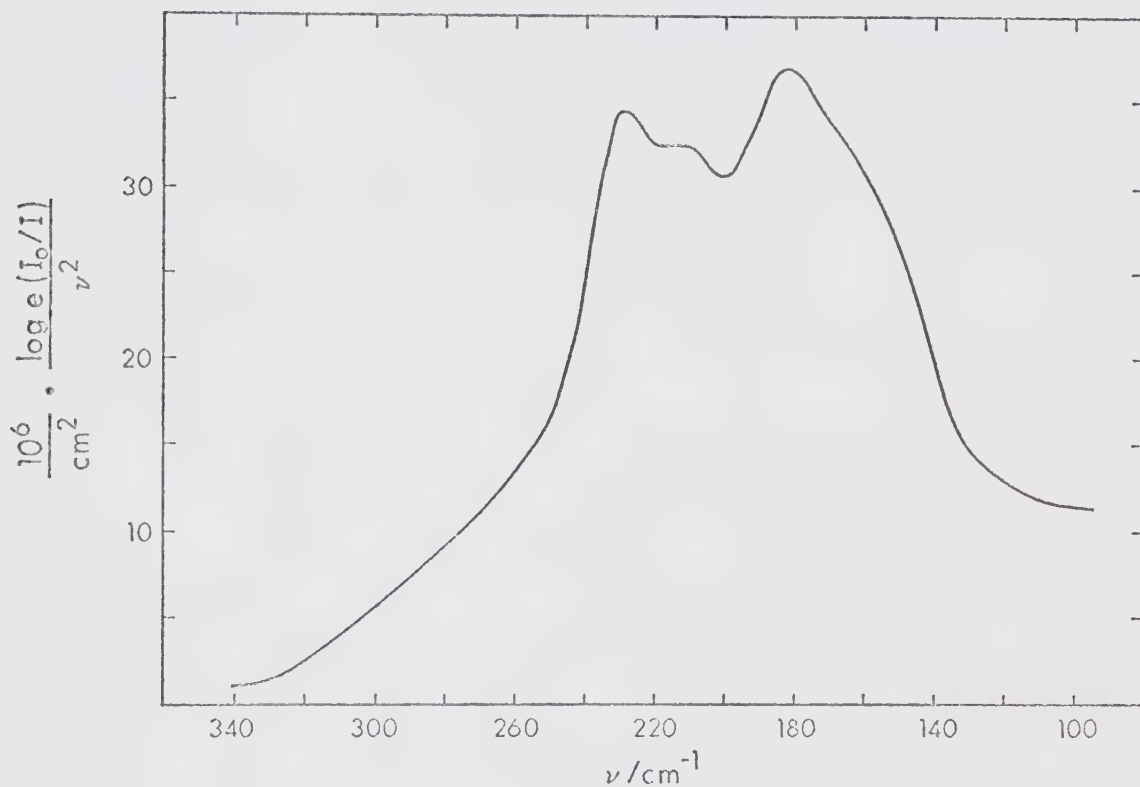


FIGURE 23. Graph of $(\log_e I_0/I) / \nu^2$ against ν for ethylene oxide hydrate at 100°K. Calculated from the unlabelled curve in the upper box of Figure 7.

possible contribution by the guest molecules in this region.

The spectrum of the hydrate, and its relationship to the spectra of other phases primarily containing orientationally disordered water molecules, can only be understood in detail in terms of the crystal structures and intermolecular forces when calculations of the dispersion curves and density of states curves become available. These calculations are both costly and time-consuming and were not carried out in the present work. The ν_T absorption cannot, therefore, be assigned or understood from a theoretical point of view. However, a comparison of the structures and far infra-red spectra of five phases formed by orientationally disordered water molecules suggests an empirical correlation between the frequencies at which strong absorption occurs and the number, length and distribution of O-O hydrogen bonds in these phases. Table VII summarizes the structural data for ices Ih (185), Ic (184), V (166) and VI (195) and ethylene oxide hydrate (81, 83) at 100°K together with the corresponding far infra-red data (175, 198, 200).

The spectra of ice Ih and ice Ic both contain a strong, rather sharp, peak centred at 229.2cm^{-1} (198). This can be related to one type of hydrogen bond, $2.75\text{\AA}$ from oxygen atom to oxygen atom. Both spectra also contain other, weaker features and it is a limitation of this proposal that they must be neglected. The spectrum

TABLE VII. ^o STRUCTURAL DATA IN Å AND FAR INFRA-RED DATA
 IN CM⁻¹ FOR ICES Ih, Ic, V AND VI, AND ETHYLENE OXIDE
 CLATHRATE HYDRATE AT 100°K.

PHASE	O-O BOND LENGTH	% IN SOLID	WEIGHTED MEAN	MEAN WEIGHTED DEVIATION	ASSOCIATED FAR I.R. FEATURES	
					FREQUENCY	WIDTH
ice Ih	2.75	100			229.2	
ice Ic	2.75	100			229.2	
ice V	2.766	21	2.797	0.021	200±10	~50
	2.781	15				
	2.782	15				
	2.798	15				
	2.819	15				
	2.820	15				
	2.867	4				
ice VI	2.773	10	2.813	0.022	187	sh. } ~50
	2.786	10				
	2.801	20				
	2.803	20				
	2.840	40			165	
ethylene oxide hydrate	2.74 ₅	9	2.77 ₁	0.025	229.6	sh. } ~70
	2.75 ₄	52				
	2.78 ₉	26			210	
	2.82 ₁	13			187	

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of ice V contains a broad peak, centred at 200cm^{-1} , with a halfwidth of approximately 50cm^{-1} (175). The frequency of the maximum can be related to the weighted mean O-O bond length of $2.797\text{\AA}$ while the breadth can be taken to reflect the relatively equal distribution of O-O bond lengths with a mean weighted deviation of $0.021\text{\AA}$. The spectrum of ice VI contains a broad peak centred at 187cm^{-1} , and a shoulder at 160cm^{-1} (200). The overall half-width of the peak plus shoulder is about 50cm^{-1} . The peak frequency can be correlated with the weighted mean O-O bond length of $2.813\text{\AA}$ while the breadth can be related to the relatively equal distribution of O-O bond lengths with a mean weighted deviation of $0.022\text{\AA}$.

The strongest feature in the hydrate spectrum is the peak at 229.6cm^{-1} . By comparison with the data on ice I, this can be related to the 52% of O-O bonds that are $2.75\text{\AA}$ long. This peak is broader than the corresponding peak in ice I and the broadening on the high frequency side can be related to the 9% of $2.74\text{\AA}$ bonds in the structure. Between about 185 and 210cm^{-1} , the hydrate absorbs more strongly relative to the 229cm^{-1} peak than does ice I and there are definite features at these two frequencies. By comparison with the data on ices V and VI, this can be related to the 26% of $2.79\text{\AA}$ bonds and the 13% of $2.82\text{\AA}$ O-O bonds in the crystal. This correlation is clearly rather approximate but the experimental data strongly

suggests that a useful correlation does exist.

It is important to note that this correlation is purely empirical and is not based on a theoretical interpretation of the spectrum. The correlation is by no means unreasonable on theoretical grounds but the detailed assignment of these features is undoubtedly more complicated than the correlation suggests.

A noteworthy difference between the spectrum of the hydrate and that of ice I is the isotope shift of the 229cm^{-1} peak. The peaks are essentially coincident in the hydrate and in H_2O ice I, but are at 223.1 and 221.7cm^{-1} in the deuterate and D_2O ice I, respectively. The ratio of peak frequencies of the hydrate to the deuterate is 1.029 , compared to the 1.054 expected from a simple harmonic oscillation model, and the 1.034 found in ice I (198). Bertie and Whalley have argued that the low ratio in ice I cannot be due entirely to anharmonicity of the translational lattice vibrations, and must reflect a smaller effective harmonic potential constant for H_2O than for D_2O . This effect is clearly even more pronounced in the clathrate hydrate structure unless the smaller isotope shift in the clathrate arises either from interaction between water molecule vibrations and guest molecule vibrations or from changes in the unit cell parameters. Interaction between host and guest molecules seems unlikely in view of the probable frequency of the

guest molecule vibrations (section 5.2). In order to check whether the unit cell dimensions for the hydrate and deuterate were the same, they were calculated from measurements of the X-ray photographs. The average unit cell parameter was $11.88 \pm 0.03 \text{ \AA}$ for the hydrate and $11.90 \pm 0.03 \text{ \AA}$ for the deuterate. The difference is clearly not statistically significant and if taken at face value is in the opposite sense to that required to explain the low hydrate/deuterate frequency ratio. However, the possible interpretation of this low isotope shift in terms of different lattice parameters cannot be completely ruled out.

Finally, the absorption above about 230 cm^{-1} in ice Ih was assigned to effects due to long range interactions (198). Two weak features were observed in ice I at 275 and 305 cm^{-1} (198) whereas in the hydrate only one feature is seen, at 300 cm^{-1} . Hence, if this assignment is correct, the long range interactions in the two systems are very similar but slight differences do exist. These results agree well with the conclusions concerning the $\nu_{\text{OH}}(\text{H}_2\text{O})$, $\nu_{\text{OD}}(\text{D}_2\text{O})$ and ν_{R} bands.

The frequencies and halfwidths of the $\nu_{\text{OH}}(\text{HDO})$ and $\nu_{\text{OD}}(\text{HDO})$ bands in ices Ih (203), V (177) and VI (200) together with those for ethylene oxide clathrate hydrate are shown in Table VIII. The ratio of the frequencies of $\nu_{\text{OH}}(\text{HDO})/\nu_{\text{OD}}(\text{HDO})$ lies between 1.35 and 1.36 for all the

TABLE VIII. THE FREQUENCIES AND HALFWIDTHS IN CM^{-1} OF THE ν_{OD} (HDO) AND ν_{OH} (HDO) ABSORPTIONS IN ICES Ih, V AND VI AND ETHYLENE OXIDE CLATHRATE HYDRATE AT 100°K .

PHASE	ν_{OD} (HDO)		ν_{OH} (HDO)	
	FREQUENCY	HALFWIDTH	FREQUENCY	HALFWIDTH
ice Ih	2445 sh.			
	~ 2417	~ 18	~ 3268	~ 30
	2395 sh.			
ice V	$2461 \pm \sim 5$	~ 80	$3350 \pm \sim 10$	~ 150
	~ 2498 sh.			
ice VI	2464	~ 70	3338	~ 120
	2500 sh.		3390 sh.	
ethylene oxide hydrate	~ 2424	~ 80	~ 3272	~ 125

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165.

ices. The value for the clathrate falls at the lower end of the range. When a graph is plotted of the $\nu_{OD}(\text{HDO})$ frequency (176, 177) against the weighted mean O-O hydrogen bond distance for these phases (81, 83, 166, 168, 172, 182, 195), Figure 24, it is found that the four points each lie within 8cm^{-1} of a straight line. This line has a slope of about $910\text{cm}^{-1}/\text{\AA}$ as compared with $600\text{cm}^{-1}/\text{\AA}$ observed for ice II, an ordered ice, using the neutron diffraction data (168), while one of the two points for ice IX, which is also ordered, lies on each line. Hence, the frequency of the $\nu_{OD}(\text{HDO})$ absorption maximum increases with increasing O-O hydrogen bond length and a rough estimate of one parameter may be obtained from the other, but no exact correlation which applies to both the ordered and disordered phases exists.

The $\nu_{OH}(\text{HDO})$ and $\nu_{OD}(\text{HDO})$ bands in the hydrate are broad and, unlike those of the ordered ices, do not exhibit the sharp features which have been related to different O-O bond distances (168, 171). This confirms that the water molecules in the hydrate are orientationally disordered. Bertie and Whalley (176) have suggested that the width of the $\nu_{OD}(\text{HDO})$ and $\nu_{OH}(\text{HDO})$ bands of ice I are associated with a small range of O-O bond distances caused by the disorder of the water molecules. Hence, the half-width of about 20cm^{-1} for $\nu_{OD}(\text{HDO})$ in ice I may be taken as characteristic of each O-O bond length indicated by

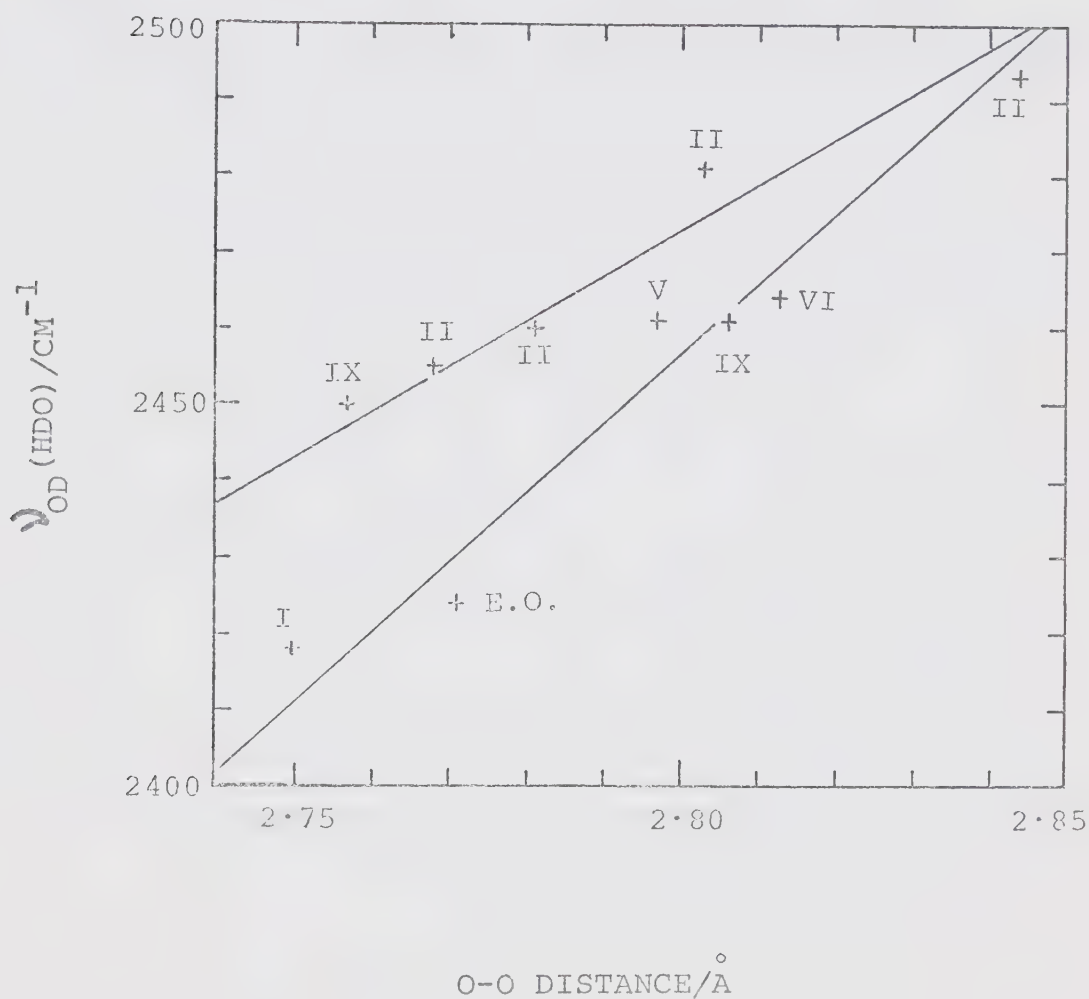


FIGURE 24. Graph of the weighted mean O-O bond distance against the frequency of the corresponding feature in the $\nu_{OD(HDO)}$ absorption for various ice phases (numbered) and for ethylene oxide hydrate (E.O.).

diffraction studies of an orientationally disordered phase. The residual halfwidths of ν_{OD} (HDO) for ice V, ice VI and the hydrate are, then, about 60, 50 and 60 cm^{-1} , and approximately reflect the mean weighted deviation of the crystallographic O-O bond lengths of 0.021, 0.022 and 0.025 Å respectively. The halfwidth for ice V seems to be high by comparison with those of the other two systems. A value of about 2300 $\text{cm}^{-1}/\text{\AA}$ for the ratio of halfwidth to mean weighted deviation of O-O bond length seems appropriate. The ranges of O-O bond distances in ices V, VI and the hydrate are 0.101, 0.067 and 0.076 Å and clearly it is less easy to correlate these with the observed halfwidths. Even when an attempt is made pictorially to account for the multiplicity of each different O-O bond length using the assumption that each crystallographically non-equivalent O-O hydrogen bond gives an absorption 20 cm^{-1} wide, it is difficult to account for these halfwidths.

5.2 Ethylene Oxide Absorption.

The frequencies of the guest absorptions in the hydrate and deuterate (Table II) are identical within 3 cm^{-1} and the shapes of corresponding bands are the same, except that the strong band at 872 cm^{-1} , with a shoulder at 881 cm^{-1} , in the deuterate is not observed as a peak in the hydrate. The largest frequency difference of 3 cm^{-1} occurs for the B_2 CH stretching mode, and a frequency difference of 2 cm^{-1} occurs for the A_2 and B_2 CH₂ rocking modes. These

168.
differences are probably associated with the difficulties of measuring the frequency of a weak peak on the side of the intense water absorption.

In view of the strong water absorption throughout the mid-infra-red region, it is important to note that the identity of the guest absorption frequencies in the hydrate and deuterate indicates that the vibrational energy levels of the guest molecules do not couple significantly with those of the host lattice. The one exception to this statement is that the strong absorption at 872cm^{-1} , with a shoulder at 881cm^{-1} , observed in the deuterate is not observed as a peak and a shoulder in the hydrate. Instead, the $\nu_R(\text{H}_2\text{O})$ absorption decreases sharply in intensity above 864cm^{-1} and a shoulder occurs at 890cm^{-1} (curve a of Figure 9). This change in the ethylene oxide absorptions due to the A_1 and B_1 ring deformations, ν_5 and ν_{12} , clearly indicates that coupling must occur between some of the rotational vibrations of the water molecules and the ν_5 and ν_{12} vibrations of the ethylene oxide molecules. It is probably significant that, although several other guest vibrations occur in the region of water molecule vibrations (Figures 5 and 6), only the ring deformations couple with them. In particular the A_2 and B_2 CH_2 rocking modes at 810 and 807cm^{-1} in the deuterate (curve a of Figure 16) are clearly observed as features on the $\nu_R(\text{H}_2\text{O})$ band of the hydrate (curve a of Figure 9) and it is not immediately

obvious why these guest vibrations should not also couple with those of the host.

Two possible mechanisms of coupling between the ν_5 and ν_{12} ethylene oxide vibrations and the $\nu_R(\text{H}_2\text{O})$ vibrations will be considered. First, a mechanical interaction due to a close approach of the guest and host atoms may occur. From X-ray data McMullan and Jeffrey (81) concluded that the shortest distances between guest and host atoms are $3.18\text{\AA}$ from guest oxygen to host oxygen atoms and $3.70\text{\AA}$ from guest carbon to host oxygen. The van der Waals radii of oxygen and the methylene group are 1.4 and $2.0\text{\AA}$, respectively (230). Hence, the guest and host oxygen atoms are within $0.4\text{\AA}$ of being in van der Waals contact and the methylene group and the host oxygen atom are within $0.3\text{\AA}$. It is, therefore, not possible to rule out mechanical interaction as the cause of intermolecular coupling, but it is difficult to understand why only the ethylene oxide ring deformation vibrations are involved. Second, interaction between the changes in dipole moment during the guest and host vibrations may occur. The magnitude of this interaction, called a transition-moment interaction, depends on the magnitude of the transition-moments of the vibrations which are, in turn, related to the intensity of absorption by the vibrations. The ν_5 and ν_{12} ethylene oxide absorptions are the strongest absorptions by the guest in the spectrum of the deuterate

(Figure 6), and the $\nu_R(\text{H}_2\text{O})$ band is extremely intense and, hence, these vibrations may well be the most likely to interact through transition-moment coupling. However, other strong ethylene oxide absorptions do occur in the neighbourhood of intense water absorptions (Figures 5 and 6) and these might also be expected to show the effects of guest host interaction. Hence, no definite conclusions as to the method of coupling can be made.

The frequencies and assignments of the fundamental vibrations of ethylene oxide in the gas and liquid phases and in the clathrate are given in Table VI. It is clear that the frequencies in the clathrate are usually closer to those of the liquid than those of the gas. The similarities are clearly seen in Figures 13 and 16. In particular, the liquid frequencies are lower than those of the gas by a maximum of 25cm^{-1} , except for the B_2 CH_2 stretching and twisting modes which are higher by about 8cm^{-1} . The frequencies of the clathrate absorptions are below those of the liquid by up to 6cm^{-1} , except for the A_1 and B_1 ring deformations and the B_2 CH_2 rocking mode which occur at frequencies higher than those observed in the liquid. The frequencies of the ethylene oxide absorptions in the clathrate are generally different from those of the solid (Table V), but the comparison is not easily made because of the factor group splitting in the spectrum of the solid (217 and Figures 10 and 16).

Hence, these comparisons indicate that the guest molecule at 100°K experiences similar forces to those which it experiences in the liquid at 200°K, and this is entirely consistent with the previous observations (125) that the guest molecule rotates at about 10^{10} c/s at 100°K. The spectra give no indication of anisotropic rotation of the guest molecule since no systematic correlation exists between the frequency shifts and the molecular symmetry species of the vibrations.

The band shapes of the ethylene oxide absorptions in the clathrate do not show any of the fine structure observed in gas phase spectra, nor do the bands show the factor group splitting of up to 10cm^{-1} observed (217 and Figure 10) in the solid. The only fine structure observed is the 1268 and 1270cm^{-1} doublet together with the two satellite peaks at 1255 and 1280cm^{-1} , shown in Figure 15. In view of the fact that the molecules have 'largest van der Waals diameter' of $5.2\overset{\circ}{\text{Å}}$ (42) and the tetrakaidcahedral cages centres are $6\overset{\circ}{\text{Å}}$ apart, and especially because the guest molecules are rotating at about 10^{10} c/s at 100°K (125) and are therefore disordered unless they rotate cooperatively, it seems unlikely that even the $1268/1270\text{cm}^{-1}$ splitting is due to factor group allowed components. Further, although there are different fields in different cages caused by the random orientation of the water molecules, Davidson has shown (130) that these

fields have a range of values with a maximum frequency of 172. occurrence close to the mean, and no other particularly probable values. Hence, it seems unlikely that these different fields would cause a specific splitting, but instead they would be expected to cause a broadening of the absorption band. The 1255cm^{-1} band is probably due to the A_1 ring breathing mode of $\text{C}^{12}\text{C}^{13}\text{H}_4\text{O}$ (217) but the 1270 and 1280cm^{-1} bands remain unassigned.

Several possible interpretations of these components of the A_1 ring stretching vibration exist. First, one or more of the absorptions may be associated with guest molecules in the pentagonal dodecahedral cages. The spectra of samples prepared by different techniques yielded no evidence to support this interpretation but the data were not definitive. Second, individual guest molecules may rotate at different speeds or may rotate anisotropically. However, the A_1 ring breathing mode occurs at almost the same frequencies in the gas, liquid and solid, 1270.3, 1268 and 1266cm^{-1} , respectively. It is difficult to understand why such rotational differences, which must be small by comparison with the differences in the molecular motion in different phases, should cause such distinct splittings. Third, X-ray results (81) have been interpreted as indicating two different equilibrium orientations of the guest in the tetrakaidecahedral cages. Dielectric results (125) indicate that the guest reorients

at about 10^{10} c/s at 100°K, and it is difficult to understand how this is consistent with the existence of just two equilibrium positions observable over the time of an X-ray study. Hence, a variety of interpretations of the splittings of the A_1 ring breathing mode are possible, but no definite experimental evidence exists to indicate which, if any, is correct.

It seems unusual that only the A_1 ring breathing mode should exhibit splitting in the clathrate, especially when it is noted that in the solid, where molecules are in van der Waals contact, this is one of the A_1 modes which does not show detectable factor group components (the A_1 CH_2 wagging mode does split) (217). However, the other vibrations of the guest which show unusual behaviour in the spectra of the clathrate are the ring deformation modes near 870cm^{-1} . In the deuterate the band at 870cm^{-1} , with a shoulder at 881cm^{-1} , is unusually broad (curve a of Figure 16) while in the hydrate, as discussed above, coupling with the $\nu_R(H_2O)$ modes occurs. It is tempting to explain the observation that all three ethylene oxide ring vibrations show more complex absorption than the other guest vibrations by postulating some form of weak interaction between the ethylene oxide oxygen atom and the host water molecules. Such an interpretation may explain why these peculiarities are confined to the ring vibrations.

This interpretation is not immediately compatible

with the observation of the very rapid reorientation of the dipole moment of the guest molecules at 100°K (125). However, the frequency of these vibrations is of the order of one thousand times that of the reorientation frequency at 100°K, while the 2cm^{-1} doublet separation is about six times greater than the reorientation frequency. It is possible, therefore, that the infra-red spectra are sensitive to an interaction that is weak enough to allow the dipolar reorientation, but strong enough to cause the effects of interaction between the ring modes and the host lattice to be observed in the spectra. But then, the different influence of this interaction on the A_1 ring stretch and the ring deformations remains to be explained fully, although it may be partially due to the close proximity of the two ring deformation frequencies.

The most obvious experimental study to clarify this problem is to observe the effect of varying the sample temperature on the spectrum. This would change the reorientation rate, and if the sample is cooled to 4°K the guest molecules essentially stop reorienting (125), thus eliminating effects due to molecular reorientation.

Most of the guest molecule absorptions are single peaks with halfwidths of 3 to 5cm^{-1} . The only exceptions to this statement are the 3069cm^{-1} band which has a half-width of about 8cm^{-1} in the deuterate (curve a of Figure 13), the $1268/1270\text{cm}^{-1}$ doublet which has an overall half-

width of about 4cm^{-1} (Figure 15) and must have a half-width of less than 2cm^{-1} for each component, and the 872cm^{-1} peak which has a halfwidth of about 7cm^{-1} in the deuterate (curve a of Figure 16). It seems likely that the 3069cm^{-1} band is broadened by the presence of the A_2 CH stretch, while the breadth of the 872cm^{-1} band with the 881cm^{-1} shoulder is less clearly understood but may be due to the guest-host interaction discussed above, or to coupling between the A_1 and B_1 ring modes in the low-symmetry environment of the clathrate. The halfwidths of the ethylene oxide bands in the liquid are all greater than 10cm^{-1} and, hence, the bands are considerably broader than those in the clathrate. Gordon (231) has suggested that the width of infra-red bands in liquids is mainly due to molecular reorientation. Bartoli and Litovitz (232) have suggested that both intrinsic and extrinsic effects are involved in the linewidth, the extrinsic effects being caused by molecular reorientation. Bertie and Sunder (233) have pointed out two factors that contribute to the intrinsic halfwidths of the absorption bands in the liquids: site effects and intermolecular vibrational coupling. The site effects arise from different fields at different sites in the liquid which cause different vibrational frequencies for molecules at these different sites. The intermolecular vibrational coupling effects arise from the close proximity of like molecules in the

liquid state, and are not expected to significantly influence the spectra of the clathrate because the closest distance between cage centres is $6\text{\AA}$ (81). In the clathrate the guest molecules reorient at a rate comparable to that believed to occur in liquids.

Two possible explanations of the sharper linewidths in the spectra of the clathrate than in those of the liquid will be discussed. First, if the orientational width is very sensitive to the speed of reorientation, then, presumably, the ethylene oxide motion in the clathrate differs sufficiently from that in the liquid state to cause a major change in linewidth. Second, molecular reorientation in the absence of intermolecular coupling may have only a small influence on the linewidth. The temperature dependence of the linewidths are required before these interpretations can be discussed further.

It only remains now to discuss the intermolecular vibrations of the ethylene oxide guest molecules. It is known from studies of the dielectric constants of the hydrate (section 1.6.2) that the ethylene oxide molecules should exhibit fairly strong far infra-red absorption. Further, it would be expected that the main contribution will come from rotational vibrations of the guest molecules. No direct assignment of these modes can be made from the spectra, partly because of the difficulty of measuring the isotope shift for the low frequency region.

Mid-infra-red spectral studies, discussed earlier, have shown that the ethylene oxide molecule experiences similar forces at 100°K in the clathrate to those which it experiences in the liquid at 200°K. Hence, by analogy with the intermolecular absorption by both non-polar (233) and polar liquids (234), the guest would be expected to show a broad absorption band centred at about 50cm^{-1} .

The intermolecular ethylene oxide absorption may be estimated from the experimental data by considering the contribution by the water molecules to the hydrate spectrum below 100cm^{-1} . Inelastic neutron scattering studies on ice I and on sulphur dioxide hydrate (131) both yield density of states curves for the water translational vibrations because the scattering from both sulphur and oxygen in the presence of hydrogen can be neglected. The results show that the density of states of water translational vibrations below 100cm^{-1} in sulphur dioxide hydrate is similar to that of ice I, except that the maximum occurs about 20cm^{-1} higher than in ice I. The far infra-red spectrum of ice I, which approximates the density of states weighted by the square of the frequency (196), has a shoulder at about 60cm^{-1} while from 100 to 60cm^{-1} the absorbance decreases with decreasing frequency and below 60cm^{-1} it decreases rapidly (198, 216). Hence, the contribution to the infra-red spectrum by the water molecule absorption in sulphur dioxide hydrate is expected to decrease from 100 to 80cm^{-1} and to decrease more sharply

below 80cm^{-1} . Presumably, an almost identical contribution to the far infra-red spectrum is made by the water molecules in ethylene oxide hydrate since both hydrates are isostructural. When such an absorption is subtracted from the observed spectrum of ethylene oxide hydrate (Figure 7) a broad band remains. This absorption extends from about 100cm^{-1} to low frequency with a maximum at about 50cm^{-1} . Thus, if these arguments are correct, the ethylene oxide intermolecular vibrations are centred at about 50cm^{-1} and contribute to the spectrum from about 100cm^{-1} to low frequencies.

Morris and Davidson (123) have estimated the frequency of the rotational vibrations of the guest molecule in the Structure II hydrates of cyclobutanone and tetrahydrofuran to be of the order of 20cm^{-1} . A similar calculation may be carried out for ethylene oxide hydrate in the following manner. The contribution, Δn , to the refractive index from a band of absorptivity $K(\nu)$ at frequency ν is given by (213):

$$\Delta n = \frac{1}{2\pi^2} \int \frac{K(\nu)}{\nu^2} d\nu .$$

Further it is known that the absorptivity is given by the equation (236):

$$\int K(\nu) d\nu = \frac{N_m \pi}{3c^2} \left(\frac{\partial \mu}{\partial Q} \right)^2$$

where c is the velocity of light, N_m is the density of

guest molecules and $\left(\frac{\partial \mu}{\partial Q}\right)$ is the change in dipole moment with respect to the normal coordinate Q . For a rotational vibration of small amplitude the simplification may be made that (123):

$$\left(\frac{\partial \mu}{\partial Q}\right)^2 \div \frac{\mu^2 \sin^2 \theta}{I \theta^2} \div \frac{\mu^2}{I}$$

where μ is the dipole moment, and I is the moment of inertia corresponding to an angular displacement θ . If it is assumed that all of the far infra-red absorption arises from the two rotational vibrations which change the direction of the dipole moment of the molecule, and if these two vibrations are assumed to be degenerate and to absorb entirely at one frequency, then, combining the above three equations the frequency, ν , of these vibrations is given in cm^{-1} by:

$$\nu = \left[\frac{N_m \mu^2}{3\pi c^2 I \Delta n} \right]^{\frac{1}{2}} .$$

For $6 \cdot 8\text{C}_2\text{H}_4\text{O} \cdot 0.46\text{H}_2\text{O}$ the unit cell is $11 \cdot 94 \text{\AA}$ at 100°K (83) which yields the density of guest molecules, N_m , as $4 \cdot 09 \times 10^{-3} \text{\AA}^{-3}$, the dipole moment of ethylene oxide, μ , is $1 \cdot 89 \times 10^{-18}$ esu cm (237) and I , taken as the mean of the two moments of inertia of ethylene oxide about the axes perpendicular to the symmetry axis, is $45 \times 10^{-40} \text{ gm cm}^2$ (143). The value of Δn may be calculated from the dielectric constants in the following manner. If the value of $\epsilon_{\omega 2}$ for ethylene oxide hydrate of $4 \cdot 1 \pm 0 \cdot 3$ (125)

is compared to the value of 2.85 for a Structure I hydrate of a non-dipolar molecule such as cyclopropane (122) then, using $\epsilon_{\infty 2} = n^2$, Δn is calculated to be between 0.26 and 0.41. These values of Δn yield frequencies of 38 and 30cm^{-1} respectively. In calculating Δn by the above method, it has been assumed that the contributions to $\epsilon_{\infty 2}$ from the electronic polarization and all vibrations other than the rotational vibrations are the same for the two hydrates. This is obviously only an approximation. An alternative method of calculating Δn is to calculate theoretically the value that $\epsilon_{\infty 2}$ would have if there were no atomic polarization (123). This method is very sensitive to the value chosen for the free radius of the cages, but if this is taken to be $2.9\text{\AA}$ (81, 123, 130) $\epsilon_{\infty 2}$ is found to be 3.2. This leads to values of the frequency that are about 44 and 36cm^{-1} , if it is assumed that the entire atomic polarization is due to the rotational vibrations. Again this is clearly an approximation and, in view of the uncertainty of the experimental value of $\epsilon_{\infty 2}$, of the approximations in the frequency calculations and of the uncertainties in the value of the free cage radius, it was not considered worthwhile to present the detailed calculations of this method. The calculations do, however, indicate that the absorption should be centred in the neighbourhood of 40cm^{-1} and from studies on other clathrate systems it seems likely that the frequency is

not significantly temperature dependent (9). Hence the calculations place the absorption at a slightly lower frequency than is obtained from the arguments based on experimental data, but in view of the complexity of the system the agreement is rather good. The calculations give no indication of the breadth of the absorption and, therefore, give no support to the deduction from experimental data that the intermolecular vibrations of the ethylene oxide molecules contribute to the spectrum up to 100cm^{-1} . It is desirable to obtain further experimental evidence on this point from the temperature dependence of the spectrum of ethylene oxide hydrate or from the spectrum of the Structure I clathrate hydrate of the non-dipolar molecule, cyclopropane, at 100°K , before a firm assignment is made.

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